

Creighton and Githens measured total vapor pressures by a static method. They determined the boiling temperatures under reduced pressures down to 75°. Their results are considerably higher than ours at corresponding temperatures and concentrations.

Kaltenbach⁶ gives graphically the boiling points of nitric acid solutions at atmospheric pressure and the composition of the vapors in equilibrium with the boiling solutions. His results for the partial pressures of nitric acid vapor appear to be lower for concentrations below the acid of maximum boiling point and higher for those above than extrapolation of our results would indicate.

Summary.

1. The total and partial vapor pressures of nitric acid solutions of concentrations approximately 20, 40, 56, 68, and 80% by weight at temperatures of 0°, 35°, 50°, 65°, and 80° have been measured.

2. From these data vapor pressures for each 10% increase in concentration and 10° rise in temperature have been calculated by graphic methods.

3. Attempts to measure the vapor pressure of 90% nitric acid were unsuccessful owing to decomposition of the acid at all the experimental temperatures except at 0°.

The authors wish to acknowledge the helpful advice of Mr. Roger Williams during the course of the investigation and the assistance of Mr. F. C. Blake in constructing the curves.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

A HIGH PRESSURE DUE TO ADSORPTION, AND THE DENSITY AND VOLUME RELATIONS OF CHARCOAL.¹

(Papers on Surface Energy and Surface Forces.)

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1. The Compression of Liquids by Charcoal.

While working on Problem 108 of the National Research Council in the year 1918 the writers discovered an interesting relationship, which is that the volume of different liquids adsorbed by the same charcoal

⁶ Kaltenbach, *Chimie Ind.*, 2, 143 (1919).

¹ Presented at the Philadelphia meeting of the American Chemical Society, September 1919. This problem was suggested to the National Research Council by the senior author. The data for one charcoal with 11 liquids were published in February 1920 (Harkins and Ewing, *Proc. Nat. Acad. Sciences*, 6, 49-56 (1920)). The present paper is an abstract of a thesis presented to the University of Chicago in August 1919 by D. T. Ewing, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

increases in the same order as the percentage compression for a definite high pressure,—such as twelve thousand atmospheres. Thus the charcoal seems to produce the same change in the volumes of liquids which penetrate it, as is given by a high pressure. In our preliminary report it was stated that while accurate calculations of the pressures which would have to be put upon these liquids to give the same percentage compressions, could not be made in the absence of data on an incompressible or very slightly compressible liquid, it seemed likely that the order of magnitude might be represented by twenty thousand atmospheres² in excess of the internal pressure of the liquid. While there is nothing novel in the idea of the existence of such powerful adhesional forces at the surface of a solid, their experimental demonstration in such a direct way is somewhat remarkable, since the highest values for the internal pressures of liquids thus far experimentally demonstrated³ are 34 atmospheres with water at 24.4°, 39.5 atmospheres for ethyl alcohol at 22.5°, and 72 atmospheres for ether at 17.7°.

Our hypothesis that the compression of the liquid is due to a pressure of this order of magnitude at the interface liquid-charcoal, is supported by the very interesting work of Lamb and Coolidge,⁴ who approach the subject from an entirely different experimental standpoint. They find that the net heats of adsorption are closely proportional to the heats of compression under high pressure, which “indicates that the liquids are all attracted by the charcoal with substantially the same force, and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres when 1 cc. of liquid is adsorbed on 10 g. of charcoal.” Still another paper,⁵ also published later than our own, comes to the conclusion that the volume of a liquid in charcoal is different from the volume of the same mass of the same liquid in bulk.

² It is obvious that the magnitude of the mean pressure decreases as the volume of liquid considered increases.

³ Donny, *Ann. chim. phys.*, 16, 167 (1846); Berthelot, *ibid.*, [3] 30, 232 (1850); Moser, *Ann. phys.*, [2] 160, 138 (1877); Helmholtz, *Ges. Abh.*, 3, 264 (1887); Worthington, *Phil. Trans.*, [A] 183, 355 (1892); Meyer, “Zur Kenntnis des negativen Druckes in Flüssigkeiten,” Halle, 1911. The heat of adsorption was discovered as a phenomenon by Pouillet nearly one hundred years ago (*Gilb. Ann.*, 73, 356 (1823)). The hypothesis that the high heat of adsorption indicates that it may be convenient to look upon adsorbed material as in a compressed state, is also very old. It is discussed in Freundlich's “Kapillarchemie” (Leipzig, 1909, p. 111). However the work of the present writers gives the first direct experimental demonstration of this compression, and shows that the magnitude of the effect is much greater than has usually been supposed.

⁴ Lamb and Coolidge, *THIS JOURNAL*, 42, 1146-70 (1920).

⁵ A. M. Williams, *Proc. Roy. Soc. (London)*, 98A, 223-34, December (1920). The writer has not been able to consult this paper since this number has failed to reach any of the Chicago libraries.

In March 1920 Cude and Hulett⁶ published data on the volume and density relations of one charcoal as obtained with four different liquids. It happened that at the time our preliminary paper giving data on 11 different liquids had been published, and we were somewhat disturbed to find that the agreement between the two sets of data was not as perfect as might have been desired, though the only discrepancy was for the single liquid benzene. However, on this account the publication of the present paper has been delayed for considerably more than a year. During this time Mr. C. E. Monroe has repeated a number of the determinations and has extended the investigation to other liquids for which the compressibilities have been determined by Bridgman. His results will be published in a separate paper, but it may be stated that they agree almost exactly with those of the present and also of the preliminary publication.

In the experiments presented here the charcoal was outgassed by the use of a mercury condensation pump with a large throat and connecting tube (25 mm. in diameter), but it was found necessary to constrict the tubes near the charcoal bulb to 1 cm. The apparatus first used was similar to that described by Lemon⁷ since we had two sets of this apparatus for work on the speed of adsorption of various poison gases. However such an elaborate apparatus is unnecessary for the work on liquids, and a system without stopcocks was found to be better for this purpose. The outgassing was first conducted at low temperatures, with a gradually increase to 600°. The tubes of charcoal were kept at the latter temperature from two to three days, or until the pressure registered by the McLeod gage had fallen to 0.0001 mm. and had remained as low as this for at least 6 hours. This pressure was determined while the pump was still running, but the tubes of charcoal were connected to the main vacuum line (1.5 cm. in diameter) between the gage and the pump. The neck of the bulb, which usually contained about 10 g. of charcoal, was then sealed off to a point while the bulb was still kept hot in the electric furnace. The bulb was cooled, the point dipped under the surface of the hot liquid, and broken off, so as to allow the liquid to rise into the tube. The tube was weighed at intervals, being kept in a thermostat at 20.00° except during the periods it was kept in the balance. The surface of the liquid was so adjusted in the thermostat that the lower part of the meniscus was exactly at a fine circular graduation made on the neck of the tube where it had been constricted to a capillary. After the drift had ceased, the final data as recorded, were obtained. The character of this drift has been treated by Cude and Hulett, and will be considered by Mr. Monroe, so only the final density data will be presented here.

⁶ Cude and Hulett, *THIS JOURNAL*, **42**, 391-401 (1920). Their results on benzene are affected by some factor which we have not been able to duplicate.

⁷ Lemon, *Phys. Rev.*, **14**, 283 (1919).

2. Apparent Density and Volume Relations of Charcoal.

The most closely agreeing data were obtained by the use of a steam activated, coconut-shell, gas-mask charcoal E 602, which gave a service time of 47.2 minutes by the accelerated chloropicrin test. On account of the close agreement of the three or more density determinations with each liquid, in general to ± 0.001 , only the average values will be included in Table I, which gives the results for this charcoal. The density listed in Col. 2, and the pore volume given in Col. 3, are not the real, but only the apparent values, calculated on the basis that the liquids are incompressible, or what amounts to the same thing in this case, that the liquids are not attracted by the charcoal sufficiently to cause any compression. Since apparently this kind of assumption is not justified, the true density and pore volume can be calculated only when the correct interpretation of the cause of the considerable variation shown in the table, is obtained.

TABLE I.

APPARENT DENSITY AND PORE-VOLUME DETERMINATIONS FOR A STEAM-ACTIVATED
COCONUT-SHELL GAS-MASK CHARCOAL.

(Charcoal E 602; service time 47.2 minutes; $-\Delta v = 0.058$ cc.)

(Data at 25°.)

1. Liquid.	2. Apparent density.	3. Pore volume 1 cc.	4. Percent compressed 12000 at- mospheres. ^a	5. Surface tension, dynes per cm. γ .	6. Viscosity in absolute units. η .	7. $\frac{\gamma}{\eta}$.	8. b . $\times 10^4$.
Mercury	0.865	57.0
Water	1.843	0.534	20.51	72.8	0.0101	7200	14
Propyl alcohol	1.960	0.559	22.93	23.7	0.0223	1062	76
Chloroform	1.992	0.566	27.13	0.0057	4760	45
Benzene	2.008	0.568	28.88	0.0064	4510	54
<i>p</i> -Xylene	2.018	0.571	28.33	0.0064	4430	81
Petroleum ether	2.042	0.579
Carbon disulfide	2.057	0.580	25.75	31.38	0.0037	8480	34
Acetone	2.112	0.590	27.0	23.50	0.0033	7120	44
Ether	2.120	0.592	30.0	17.1	0.0024	7125	39
Pentane	2.129	0.593	More than ether	About 15	0.0024	6200	65

^a The solubility of gases in these liquids increases in *general* with the percentage of compression or the compressibility, but the order is not exactly the same. The values for the density and for the pore volume listed in this table are calculated on the basis of the incorrect assumption that the liquids are incompressible. The same values would be obtained if the liquids are compressible but are not compressed. The eighth column gives the values of *b* of van der Waals' equation.

TABLE II.

APPARENT DENSITIES OF EIGHT CHARCOALS IN WATER, MERCURY AND VARIOUS ORGANIC LIQUIDS.					
Charcoal.	Liquid.	Apparent density.	Mean apparent density.	Volume of carbon in 1 cc. of charcoal.	Volume of pores in 1 cc. of charcoal.
Charcoal A (Steam activated, coconut shell-charcoal; impregnated with copper; service time = 42.9 minutes; $-\Delta v = 0.052$ cc.)	Hg	0.843
	Hg	0.841	0.842
	H ₂ O	2.112
	H ₂ O	2.112	2.112	0.399	0.601
	C ₆ H ₆	2.291
	C ₆ H ₆	2.298	2.295	0.366	0.643
	Ether	2.432
	Ether	2.422	2.426	0.347	0.653
Active carbon No. 4 (From anthracite coal and pitch; service time = 40.9 minutes; $-\Delta v = 0.067$.)	Hg	0.705
	Hg	0.713	0.709
	H ₂ O	1.807
	H ₂ O	1.809	1.808	0.392	0.608
	Ether	2.186
	Ether	2.172	2.177	0.325	0.675
Charcoal No. 1 (Air activated, coconut-shell charcoal; service time 32 minutes; $-\Delta v = 0.053$ cc.)	Hg	0.869	0.869
	H ₂ O	1.863	1.863	0.467	0.533
	C ₆ H ₆	2.014	2.014	0.432	0.568
	Pet. Eth.	2.042	2.042	0.421	0.579
	Ether	2.094	2.094	0.414	0.586
E621..... (Air activated, coconut-shell charcoal; service time = 27 minutes; $-\Delta v = 0.051$.)	Hg	0.989
	Hg	0.998	0.995
	H ₂ O	1.832
	H ₂ O	1.838	1.835	0.542	0.458
	Ether	2.023
	Ether	2.029	2.026	0.491	0.509
Active carbon No. 1 (from anthracite coal and pitch; service time = 19 minutes; $-\Delta v = 0.043$ cc.)	Hg	1.177
	Hg	1.172	1.175
	H ₂ O	1.936
	H ₂ O	1.932	1.934	0.609	0.391
	Ether	2.076
	Ether	2.074	2.075	0.566	0.434
Active carbon No. 3 (from anthracite coal alone; service time = 11 minutes; $-\Delta v = 0.018$ cc.)	Hg	1.488
	Hg	1.492	1.490
	H ₂ O	1.880
	H ₂ O	1.872	1.876	0.799	0.201
	Ether	1.911
	Ether	1.902	1.906	0.781	0.219
Laboratory charcoal (from beechwood; service time = 0.0 minutes; $-\Delta v = 0.004$ cc.)	Hg	0.521	0.521
	H ₂ O	1.644	1.644	0.317	0.683
	Ether	1.665	1.665	0.313	0.687

TABLE II (Continued).

Charcoal.	Liquid.	Apparent density.	Mean apparent density.	Volume of carbon in 1 cc. of charcoal.	Volume of pores in 1 cc. of charcoal.
Cedar wood (service time = 0.0 minutes; - Δv = 0.008 cc.)	Hg	0.817
	Hg	0.813	0.815
	H ₂ O	1.497
	H ₂ O	1.502	1.499	0.544	0.456
	Ether	1.504	1.504	0.536	0.464

In order to understand the volume and density relations upon which the adsorptive properties of charcoal depend, it is important to obtain an idea of the structural relations of coconut charcoal, insofar as the latter can be revealed by the use of the microscope. The writers have about 60 microphotographs, with magnifications as high as 2000, prepared by Dr. Rheinhardt Thiessen of the U. S. Bureau of Mines, and these have been used in the present study of the pore volume relations. Unfortunately none of these can be presented here, but reference may be made to three microphotographs reproduced in an earlier paper by Lamb, Wilson, and Chaney,⁸ which do not, however, represent all of the types of structure found. A reference to their Figs. 7 and 8 (pp. 428 and 429) of their paper will show that the lumps of charcoal contain many pores which are visible at a magnification of 732 diameters. Those visible at a magnification of 2000 may be called capillaries or macropores. The walls of carbon, which are represented by the light portions of the figure, are undoubtedly very porous, and contain an enormous number of "micropores" which are ultramicroscopic. A study of the photographs shows that the mean diameter of the macropores is about 12 microns.⁹ The micropores may be defined arbitrarily as those whose diameters are less than 10^{-5} cm. (less than 100 millimicrons), though vapor-pressure measurements indicate, insofar as they are of any value for this purpose, that they are mostly of the order of 10^{-6} cm. or less, in diameter.

Since mercury penetrates neither the capillaries nor the micropores, the density given in Tables I and II, with this liquid used to fill the "voids" between the lumps of charcoal, is that of the lumps themselves, walls, micropores, and capillaries included, or what is known as the lump or "block density." It will be seen that this density is close to 0.85 for two of the highly activated coconut-shell charcoals, but is considerably higher for the slightly activated charcoal E 621, for which the value is practically 1.000. The density of the cedar wood charcoal, 0.815, is very nearly the same, yet this specimen shows an almost zero service time, while beechwood charcoal, also a very poor adsorbent, has a block density of only 0.521. The active carbon 4, with a moderately high service time of 40.9 minutes, has a moderately low density (0.709), and the much

⁸ Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, 11, 420-38 (1919).

⁹ This diameter is dependent upon the methods of production of the charcoal.

less active No. 1, also made from anthracite coal and pitch, has a much higher density (1.175), while the still less active carbon No. 3, with the low service time of 11 minutes, has a very high density (1.490).¹⁰

3. Relation of the Total Apparent Pore Volume to the Compressibility of the Liquids.

The most remarkable feature of Tables I and II is that the apparent density and total pore (capillary and micropore) volume depend upon the liquid in which the charcoal is immersed, and in general both increase markedly either as the compressibility increases or the viscosity decreases. This suggests alternative hypotheses, which lead to practically opposite conclusions with respect to the density. The first of these, supported also by the later data obtained by Mr. Monroe, is that *the liquid in the micropores is very highly compressed by adsorption, and that this compression is greater, the greater the compressibility of the liquid in bulk.*¹¹ That the molecules of the liquid should be drawn closer to the atoms in the surface layers and edges, seems to be the normal supposition when the magnitudes of the adhesional forces are taken into account, since such forces are much more intense than those which hold the molecules of liquid together. While this may not have been proved directly, it is evident that the energy of adsorption for a charcoal surface is very much higher than the energy of cohesion in water or in an organic liquid, since the energy of vaporization of such an adsorbed liquid is very much greater than that of the liquid itself. In addition to this the work of this laboratory has shown that even on a mercury surface the energy of adhesion for these liquids is usually three or more times that in the pure liquids. It should be noted that this factor is altogether too low to express the relations at a carbon surface.

However, the compressive effect need not vary directly as the compressibility of the liquid in bulk, since the liquid is not compressed isotropically. A second factor which might be expected to cause a divergence is that the force of adhesion is not the same for all of the liquids. When these factors are considered, the agreement in the order seems very remarkable.¹²

When the highly evacuated lump of charcoal is put under the surface of a liquid, the latter enters the capillaries or macropores, and these in the charcoals which preserve to a considerable extent the original structure of the shell, have diameters of the order of 0.012 mm. in diameter, so they are filled quickly, provided they are in direct communication with the

¹⁰ All of these data refer to the lump density.

¹¹ The second hypothesis suggested, that the most viscous liquids penetrate least, does not seem to be in good agreement with the experimental data, as indicated later in the text.

¹² This indicates that the variation of the adhesive force with a change from water to various organic liquids, is not very great. This agrees with the conclusion of Lamb and Coolidge (Ref. 4).

liquid, but the micropores are filled much more slowly. In the capillaries the driving force of penetration is the surface tension, while the retarding force is the viscosity, and the speed of penetration should vary as the ratio γ/η where γ represents the surface tension and η the viscosity. That this is true has recently been shown by Washburn. It might be thought that the differences in the volumes of the liquids which penetrate the charcoal are due to incomplete penetration by some of the liquids, especially in the cases of water and propyl alcohol, but there is *no parallelism* between the values of the ratio $(\gamma/\eta)^{1/2}$ and the volume of liquid which penetrates. However, as the pores become finer the influence of the viscosity may become predominant, especially when the liquid after passing through a part of a narrow pore enters into a region where its cross section becomes enlarged.

While a consideration of the relation between the pore volumes and the viscosities of the liquids as presented in Table I, shows that the data would in general support the idea that the effects might be due to different penetrations of the charcoal by the different liquids, the least viscous penetrating most, it will be seen that the propyl alcohol is very badly out of order in this sense, though in exactly the order prescribed by the compressibility hypothesis. Since several other liquids have been found by Mr. Monroe which are also out of order with respect to viscosity, but in the order of the compressions, it seems evident that at least the greater part of the observed differences in volume is due to the compression of the liquid, though the viscosity may exert a minor influence upon them.

The apparent densities in water of the coconut-shell charcoals as given above are 1.843 and 1.863; that of the similar charcoal used by Titoff, 1.86; by Baerwald, 1.92; and by Miss Homfray, 1.66; by Cude and Hulett, 1.854 on 18- to 20-mesh, and 1.900 for the same charcoal of 100- to 200-mesh (per inch). Kerosene gave very nearly the same apparent density with charcoal E 602 as benzene, or about 2.008. With this may be compared the data obtained by Chaney and Apmann, who determined the apparent density in kerosene of 30 charcoals, and found that the lower the value of this quantity, the lower in general is the service time. Thus densities in kerosene of 2.14, 2.17, 2.11, 2.11, 2.08, 2.02 and 2.02, correspond respectively to service times of 68, 64, 60, 59, 57, 55, and 54 minutes; while at the other extreme, densities of 1.98, 1.86, 1.87, 1.66, 1.63, and 1.66, correspond to service times of 33.1, 30.7, 27.6, 17.8, 8.0, and 4.3 minutes. Their data are in good agreement with the value found here, since a density of 2.02 in kerosene, the value corresponding to Table I, was found by them to correspond to a service time of 41 to about 49 minutes, which is not very far from that given in Table I.

However, there is not such good agreement with the data obtained by Cude and Hulett,⁸ as is shown in Table III.

TABLE III.

APPARENT DENSITIES OF TWO SPECIMENS OF COCONUT-SHELL CHARCOAL.

Liquid.	Cude and Hulett charcoal A 909 (18- to 20-mesh).	This investigation charcoal E 602 (10- to 14-mesh).
Water	1.854	1.843
Benzene	1.797	2.008
Carbon disulfide.....	1.915	2.057

The discrepancy in the sign of the difference exists only in the single case of benzene. This liquid exhibited the same relative order in our investigations of two other charcoals, A and No. 1, so its position in the series can hardly be an accident, especially as many determinations were run for charcoal E 602. Some factor was evidently present in the work of Cude and Hulett,⁶ which was absent in our own. It is possible that the discrepancy is due to the extent of the outgassing, which was more thorough in our work, since we happened to have a very much more rapid vacuum pump, used a large connecting tube in place of their capillary, and outgassed for 3 days.

It is of interest to note that in the more active charcoals the apparent volume of ethyl ether, minus the volume of water, in the pores of 1 cc. of charcoal ($-\Delta v$),—which shows how much more the ether is compressed than the water,—is nearly constant and about 0.055 cc. as is shown by Table IV.

TABLE IV.

COMPRESSION OF ETHER IN CUBIC CENTIMETERS PER CUBIC CENTIMETER OF CHARCOAL, MINUS THE COMPRESSION OF WATER ($-\Delta v$).

Charcoal.	Service time, minutes.	$-\Delta v$.
E 602	47.2	0.058
Rankinite A	42.9	0.052
Active carbon 4	40.9	0.067
Charcoal 1	32.0	0.053
E 621	27.0	0.051
Active carbon 1	19.0	0.043
Active carbon 3	1.10	0.018
Cedar wood charcoal	0.0	0.008
Beechwood charcoal	0.0	0.004

Of these charcoals the last, that made from beechwood, was the poorest adsorbent for chloropicrin as determined by the regular test. It is apparent that the value of $-\Delta v$ is nearly constant as the service time decreases from 47 to 27 minutes, but falls very rapidly as the service time decreases to 19 and 11 minutes, while the charcoals which give practically a zero service time, give also a very small value for the compression decrement ($-\Delta v$).

4. The Heat of Adsorption of Liquids in Charcoal.

When lumps of outgassed charcoal are dropped into a liquid, or when a liquid is poured into a tube which already contains the charcoal, the liquid

penetrates the charcoal, with the result that the carbon surface of the pores disappears, and a carbon-liquid interface takes its place. In this process heat is developed, and this may be specified as the heat of immersion, of adsorption ($-Q_a$), or of absorption. Thus 1 g. of bone charcoal, which had not been outgassed, gave off 18.5 calories when immersed in water, while the same weight of fuller's earth in the same liquid, gave 32 calories. The data of Lamb and Coolidge on the heat of adsorption of vapors by charcoal, indicate that the heat of immersion of a typical coconut-shell charcoal in carbon disulfide is of the order of 35 calories per gram.

The heat of immersion of a solid whose surface is so nearly plane that its surface energy is essentially equal to that of the same area of a plane surface of the same material, or the heat of adsorption of a liquid on the surface of the solid, may be defined in a corresponding way as the amount of heat liberated ($-Q_a$) when a solid with a surface of this type, and of an area of 1 sq. cm. is immersed in a liquid in such a way as not to increase materially the area of the surface of the liquid. In this process the surface of the solid would disappear, and in its place would appear the same area of interface solid-liquid. The heat liberated ($-Q_a$), would be equal to the total amount of energy given off in the process when carried out isothermally (E_a), and this is equal to the total surface energy of the solid (E_s), minus the total surface energy of the interface (E_i), for 1 sq. cm. of surface. Since the total surface energy is always equal to the free surface energy (γ) plus the latent heat of the surface ($-T \frac{\partial \gamma}{\partial T} = l$), the following equation expresses the value of the heat of adsorption.

$$-Q_a = E_a = E_s - E_i = \gamma_s + l_s - (\gamma_i + l_i) = \gamma_s - T \frac{\partial \gamma_s}{\partial T} - \gamma_i + T \frac{\partial \gamma_i}{\partial T} \quad (1)$$

It is obvious that this equation is also valid for the heat of immersion of a liquid, or for the heat of adsorption of one liquid on the surface of another liquid, so in its more general sense the subscript s refers to the phase whose surface is already developed, but later disappears, giving place to an interface of the same area. The heat liberated on the immersion of a solid has always been found to be a positive quantity, which indicates that the total interfacial energy per unit area is always less, so long as this holds true, than the total surface energy of the solid. That this is not always the correct sign of the effect, at least when only liquids are involved, is shown by the fact that hexane, octane, and carbon tetrachloride have negative heats of immersion in water equal respectively to -0.21 , -0.21 , -0.26 , times 10^{-6} calories per sq. cm. at 20° , though the heats of immersion of water in these liquids are all positive, 1.4, 1.34, and 1.05 times 10^{-6} calories per sq. cm. Even in the case of two liquids heat is almost always evolved on immersion as the result of the surface energy changes. Thus, for example, the heat of immersion of normal octyl

alcohol at 20° in water is 1.28, and of water in octyl alcohol, 2.85, in terms of the units used above.

The heat liberated on adhesion ($-Q_A$), and the total adhesional energy (E_A), are always larger positive (or smaller negative) quantities than those which give the heat liberated on immersion (heat of adsorption), provided the surfaces are plane. The following equation gives the heat of adhesion.

$$-Q_A = E_A = E_s + E_l - E_i = (\gamma_s + l_s) + (\gamma_l + l_l) - (\gamma_i + l_i) \quad (2)$$

These are the same as the heat and energy of approach, since the surfaces of two phases already in existence, approach each other and disappear, while an interface, equal in area to that of either surface which disappears, takes their place. The heat of adhesion is 2.6 for water-hexane, 4.0 for water-octyl alcohol, 2.5 for water-carbon tetrachloride, all in 10^{-6} calories per sq. cm. at 20°.

When a liquid spreads over a solid, the surface of the solid disappears, while an interface of the same area appears. If the solid has a plane surface, then a liquid surface of the same area also appears; so, provided the liquid layer is not too thin, the following equation holds

$$-Q_{sp} = E_{sp} = E_s - (E_l + E_i) = \gamma_s + l_s - (\gamma_l + l_l) - (\gamma_i + l_i) = E_A - E_c$$

where E_c represents the energy of surface cohesion of the liquid.

Obviously

$$-Q_a = E_a = E_A - E_l$$

or the heat liberated by the adsorption of a liquid equals the energy of adhesion minus the surface energy of the liquid. Also

$$-Q_a = E_a = E_{sp} + E_l.$$

and

$$E_{sp} = E_A - 2E_l.$$

The heat of adsorption of a saturated vapor is

$$-Q_g = (\gamma_s + l_s) - (\gamma_i + l_i) + \lambda v = E_s - E_i + \lambda v$$

where $-Q_g$ is the heat of adsorption of enough vapor to form a liquid in bulk covering the solid surface at constant temperature, and λ is the latent heat absorbed in the vaporization of the liquid per unit volume of vapor. It is assumed here that the area of the surface of the liquid formed is negligible in comparison with the area of the interface which is formed.

While we do not have the values of the above quantities for carbon, they have been determined in this laboratory for the interfaces between mercury and other liquids; in which case the values for the liquid mercury may be substituted for the values for the solid in the above equations. The heat of adsorption as defined above is thus found to be 3.25 for *iso*-butyl alcohol, 2.60 for *secondary* octyl alcohol, and 3.13 for octane, all

in 10^{-6} calories per sq. cm. The heat of spreading of *n*-octyl alcohol on water is about that of *iso*-butyl alcohol on mercury, but that for octane on water is less than half the similar value for mercury.

5. The Area of the Surface Exposed to a Liquid inside One Gram of Charcoal.

That there is anything in a lump of charcoal which corresponds to a plane surface is altogether improbable; and it is not unlikely that what corresponds to a surface may be molecularly rough, so that it would be impossible to designate any number which would correspond to the area in square centimeters of the surface. However, several estimates of this surface area have been made. Thus Lamb, Wilson, and Chaney⁸ have estimated the surface in 1 g. of an activated charcoal as 1000 square meters, Lowry and Hulett¹³ obtain the value 200 square meters for a similar charcoal, while A. M. Williams,¹⁴ in developing a new interpolation formula for the adsorption of gases, calculated the surface of the non-activated charcoal used by Miss Homfray as 131 square meters.

The data given in the preceding section of this paper, together with the equations given there suggest an independent method of determining whether these estimates are of the right order of magnitude to represent what may be called the "apparent surface," which will be defined as the area of the plane surface of the same material which will give the same heat of immersion or of wetting when wet by the same liquid in bulk. Unfortunately for our purpose the heat of adsorption of charcoal has been determined in none of the liquids given there, so what will be presented here will be merely illustrative of the method. We will suppose that the heat of immersion of charcoal in carbon disulfide is as large or larger than the heat of immersion of mercury in octane, which does not seem unreasonable. If we assume that these two heats of immersion or of wetting are equal, the heat of immersion of one gram of charcoal in carbon disulfide, 35 calories, would correspond to an *apparent area* as defined above of about 120 square meters. Since it is practically certain that the heats of immersion of carbon are higher than those for mercury, this result would seem to represent a maximum which is still too large. The method of calculating the area of the charcoal surface by the use of the capillary equation of Anderson¹⁵ cannot be expected to give any real correspondence with even such an apparent area, since his equation obviously breaks down completely at the diameters of the micropores which are calculated from the equation. Thus Lowry and Hulett¹³ by using his equation find 1.6×10^{-8} cm. as the minimum, and 8.3×10^{-7} cm. as the maximum diame-

¹³ Lowry and Hulett, *THIS JOURNAL*, **42**, 1393-1419 (1920).

¹⁴ A. M. Williams, *Proc. Roy. Soc. Edinburgh*, **39**, 48-55 (1918).

¹⁵ Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

ters of the pores in all of the charcoals investigated by them; and calculations from data obtained in this laboratory give values of the same order but without the above minimum. These dimensions are of such a small magnitude as to approach so closely molecular dimensions, that an equation such as the one cited, developed from the relations in a capillary tube of ordinary dimensions is altogether without meaning. However, if the lower limits for the diameter at which it is still valid could be determined, it would be useful in calculating how much of the liquid is contained in pores of that and smaller diameters. Experimental work of the heat of immersion of porous solids in liquids was begun in this laboratory several years ago, but was interrupted. It will be resumed in the coming summer.

6. Volume of the Pores, and the Density of Charcoal.

If either charcoal E 602 or No. 1, for which the data are very nearly identical, is taken as a characteristic coconut-shell charcoal, it may be easily seen that if the liquids are compressed by the charcoal, the total pore volume is less than even the volume of the least compressible liquid which enters the pores, when the latter is measured before the penetration occurs, as was done in the experiments. Thus the total pore volume for E 602 is less than 0.534 cc. per cc., and in the case of No. 1 it is less than 0.533. Since the macropores have diameters of the order of 1.2×10^{-3} cm., it is evident that in them the liquids are not materially compressed, so practically the whole of the compression occurs in the micropores.

Experiments upon the adsorption of benzene show that these charcoals adsorb about 0.39 cc. of liquid benzene, 0.35 cc. of water, 0.41 cc. of ether, etc., as measured before adsorption. From this result, together with the data on the adsorption of liquids it may be calculated that the volume relations for these charcoals are approximately 0.54, 0.28 and 0.18 for the volume of carbon (volume not occupied by liquid), volume of micropores, and volume of macropores, respectively.

These values give a density of 1.60 for the active charcoal. It may be noted that the two specimens of wood charcoal which showed almost no compressive action on the liquids, those from beech and cedar wood, had densities equal to 1.65 and 1.50 respectively, or not far from the estimated value for the carbon in the coconut-shell charcoal.

While Table I does not give any values for liquids whose percentage compressions have been determined directly at 12,000 atmospheres as lying between that of propyl alcohol and that of carbon disulfide, the determinations on the compressibility of liquids at lower pressures indicate that chloroform, benzene, and *p*-xylene are in the proper order. Mr. Monroe's paper will remedy the apparent deficiency, since he has determined the pore volumes for 5 liquids which lie in this range; amyl alcohol, *isobutyl*

alcohol, ethyl iodide, and ethyl and methyl alcohols. His results give extremely strong additional evidence in favor of the compression hypothesis here presented.

7. The Small Effects of the Size of the Molecules, and of Unequal Adhesional Attractions.

Calculations made on the relation between the lowering of the vapor pressure produced by charcoal and the size of the micropores indicate such small dimensions for the latter as to suggest that the size of the molecules might be an important factor in determining the amount of liquid which will enter them. This idea occurred to the writers early in the work, and was suggested to them repeatedly by others. However, although a number of liquids were chosen with the purpose of varying the molecular size considerably, this effect is not so large that it has been possible to detect it as yet. In this connection a determination of the pore volume was made with mesitylene, a liquid whose molecules are very large. For the liquids used the values of b of the van der Waals' equation varied from 14×10^{-4} for water to 88×10^{-4} for mesitylene, which indicates a considerable variation in molecular size. Also it would seem that the force of compression might vary with the nature of the adsorbed liquid, which would indicate that the percentage compressions considered should not be taken at a fixed pressure as was done in Table I. It is evident from the data published here, and even more so from other data to be published later, that these two effects considered in this paragraph are so small as to be obscured by the compression itself.

Summary.

1. This paper gives evidence in favor of the hypothesis proposed earlier by the writers, which is that *the liquids which penetrate into charcoal are compressed by the action of a force, due to molecular attraction, which acts as a pressure of many thousand atmospheres.* In the earlier paper it was estimated that the pressure corresponded to twenty thousand atmospheres or more. The present paper indicates that it is the liquid in the micropores and not in the macropores which is compressed. On this basis the pressure would probably be considerably higher than the previous estimate, since at that time only the total pore volume was known and considered. Not only charcoal, but also all other porous substances, such as porous ceramic materials, and also very fine powders, should exert this compressive effect, but in general to a much smaller extent. The remarkable feature of the experiments listed is that they demonstrate the compression by direct measurements of the volume changes in the liquids. Experiments on the internal pressure of liquids have not succeeded in demonstrating pressures higher than 72 atmospheres.

2. Ether, which is much more compressible than water, occupies a volume *in the charcoal* which is about 10% less than that occupied by the amount of water which is, *outside the charcoal*, equal in volume to the ether. It seems probable that the water in the micropores is compressed by about 25%, or even more, while the ether is compressed by about 40%. It is evident that the liquids in the macropores, of the order of 1.2×10^{-3} cm. in diameter, are not compressed sufficiently to produce any noticeable effect upon the volume.

3. The true volume relations in 1 cc. of a characteristic coconut-shell charcoal may be estimated as: volume of micropores, 0.28 cc.; of macropores, 0.18 cc.; of carbon, 0.54; which gives a density of about 1.60 for the carbon. The density of the lumps of such a charcoal is about 0.868, though this lump or "block" density is as high as 1.49 for a charcoal made from anthracite coal, and as low as 0.52 for a wood charcoal.

4. The charcoals which are inactive as adsorbents of gases do not exert a compressive effect upon the adsorbed liquids of a sufficiently great magnitude to be very evident, though there seems to be a slight effect of this nature.

5. The densities of the carbon in the two inactive wood charcoals investigated are 1.65 and 1.50, which is not very far from the estimated density for the carbon of the active charcoals. It is evident that charcoals from which the hydrocarbons have been imperfectly eliminated, may have much lower densities still.

6. When coconut-shell charcoals alone are considered it is found that in agreement with the data obtained by Chaney and Apmann, the lower the apparent density in an organic liquid, the less is the adsorptive action on vapors. The present investigation indicates that this relation may be expected to hold the better the more compressible the liquid which is absorbed, so either ether or pentane or another highly compressible liquid should be used in such tests.

7. Simple thermodynamic equations are given for the heat of immersion or adsorption of a plane surface. While there is probably no definite area of surface inside a lump of charcoal, a definition for an "apparent area" may be given. The one chosen here is that the "apparent area with respect to the heat of immersion" is the area of the plane surface of carbon which will develop the same amount of heat on immersion as is equal to that developed by the immersion of 1 g. (or 1 cc., if such a different unit is preferred) of the charcoal in the same liquid. Since the "film" *in the charcoal* is probably a number of molecules deep, this apparent area is probably larger than corresponds to the carbon surface. Nevertheless, this method of consideration gives rise to a lower estimate of the area than the others which have been given in the literature. Thus it is in-

dicated that the apparent area defined in this way is less than 120 sq. meters per gram of charcoal.

8. The magnitude of the heat of immersion of liquids on mercury is 3.13×10^{-6} calories for octane and 3.25×10^{-6} calories per sq. cm. for *iso*-butyl alcohol.

The next two papers of this series will present additional data similar to those given here, and also on the amounts of different vapors adsorbed by the charcoals used in this investigation. These data will make it possible to calculate in much more detail the pressure and cohesional relations involved.

The writers wish to thank Mr. Chaney for preparing several special charcoals for use in this work, and to express their indebtedness to the Wolcott Gibbs Fund of the National Academy of Sciences for a grant which was used in the purchase of vacuum apparatus. While the grant was made for researches upon the cobalt ammines, the apparatus was diverted from this latter work during the war period.

The compressibility data used in this paper are those of Bridgman.¹⁶ Without the results of his remarkable investigations at high pressures, the evidence in favor of the compression hypothesis developed by the writers would have been much less convincing.

Note added Oct. 26, 1921.

Washburn¹⁷ has devised a method for determining the "true" volume of the pores in a ceramic material by the use of a gas, such as hydrogen or helium, as the fluid for filling the pores. This method has been tried in this laboratory, and has been found to be much less simple when applied to charcoal, but it will undoubtedly give consistent results when sufficient care is taken. The data obtained thus far will not be published until they are more carefully verified. With accurate data of this nature it may be possible to calculate more exactly the pore volume and the density of charcoal, though, on account of the small size of the molecules of helium the volume of the pores penetrated by this gas may be greater than that penetrated by the larger molecules of an organic liquid. Also it seems apparent that even at ordinary temperatures the density of the helium gas is not the same in the micropores as in the free gas, that is, there is a small amount of adsorption.

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¹⁶ Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 3-114 (1913); **48**, 309-362 (1912).

¹⁷ Private communication from Professor E. W. Washburn. Note added October 26, 1921.