The Swelling of Charcoal. Part I.—Preliminary Experiments with Water Vapour, Carbon Dioxide, Ammonia, and Sulphur Dioxide.

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The experiments of Meehan[*] having shown that charcoal increases in volume when taking up carbon dioxide, it became an obvious step to correlate this expansion with the quantity of gas adsorbed.[†] In this paper a form of extensometer is described which, while sufficiently sensitive and accurate for the measurement of the percentage linear expansion (x) of a rod of wood charcoal, was yet compact enough to permit its being sealed up in an all-glass apparatus, so that simultaneous determinations could be made of the weight (s) of gas taken up per unit weight of the adsorbent.

The graphs obtained by plotting the variables x and s have certain interesting characteristics which it will be convenient to describe before dealing with the detailed results. As fig. 1 shows, the coefficient dx/ds increases steadily with s; thus far the charcoal behaves similarly to many of the common gels, which contract proportionately less in the later stages of drying, owing to the micellæ coming in contact with each other. The swelling of charcoal, however, appears to follow a more regular course than that of the elastic gels, and in the case of ammonia, carbon dioxide, and sulphur dioxide is given within the limits of accuracy of our experiments by hyperbolic equations of the type

$$x = k \frac{s}{S - s} \ldots$$

where k and S are constants characteristic of each gas. In fig. 1 the experimental values of x have been plotted (for convenience of representation) against s/S. The smooth curves for ammonia, carbon dioxide, and sulphur dioxide are the graphs derived from equations of the above form, using appropriate values of the constants. An additional term (a small additive constant over the experimental range) is necessary to represent the behaviour of water vapour.

[*] Meehan, ' Proc. Roy. Soc.,' A, vol. 115, p. 199 (1927).

[†] Bangham and Fakhoury, ' Nature,' vol. 122, p. 681 (1928). The relation between the expansion and the sorption there given was not confirmed when the experiments were extended to cover a wider range of values.

The values of the constants k and S for the four gases are set out in the following table; they refer in all cases to experiments carried out at room
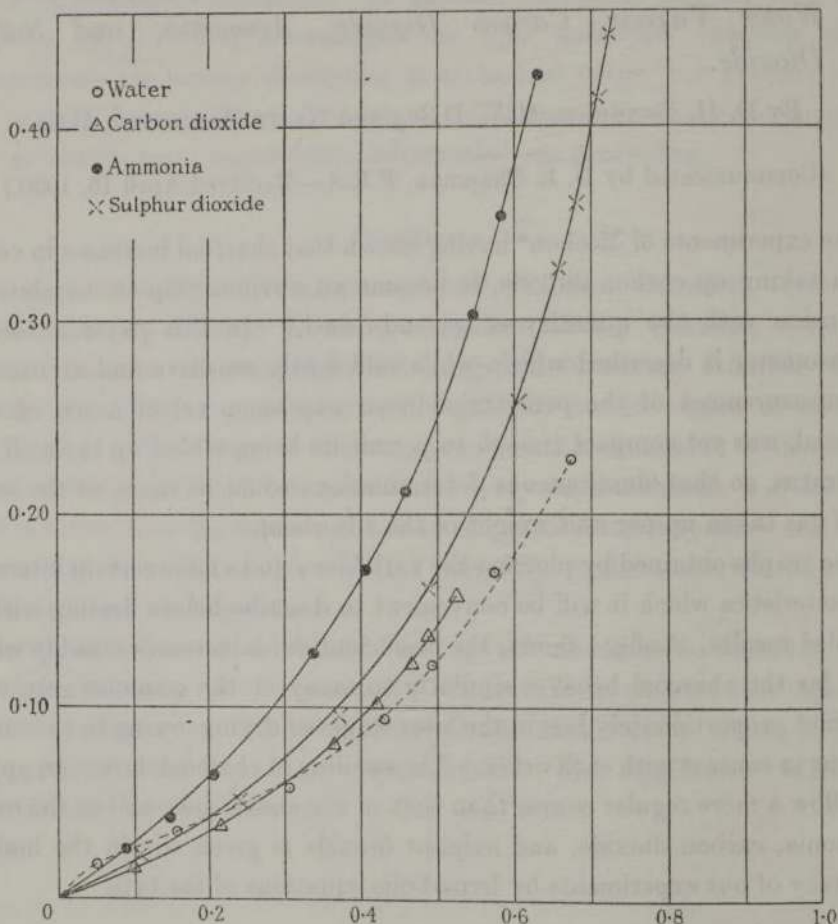

FIG. 1.—Expansion of Charcoal at Room Temperature. Abscissæ, Fractions of Limiting Sorption Values, Ordinates, Linear Expansion per cent.

temperature. It is noticeable that the S-values (which are calculable from the observations to within a few per cent.) show approximate agreement with the regularity observed by Gurvitsch* in the case of the saturation sorption values, that is to say they represent nearly equal volumes of the normal liquid at the experimental temperature. The product SV_s (where V_s is the specific volume of the liquid adsorbate) is, however, rather smaller in the case of the denser liquids.

* Gurvitsch, ' J. Russ. Chem. Soc.,' vol. 47, p. 805 (1915).

Table I.

(Temperature 18° to 20° C.)

—	H_2O.	CO_2.	NH_3.	SO_2.
k (per cent.)	0·110	0·143	0·252	0·1705
S (grams per gram of charcoal)	0·158	0·139	0·112	0·210
SV_s (cubic centimetres)	0·158	0·177	0·183	0·151

Experimental.

The extensometer used was a nickel instrument constructed to the authors' design by Messrs. Becker & Co. It operated on much the same principle as that employed by Meehan, but a scale and pointer were substituted for the optical lever. The charcoal rod was placed between the adjustable jaws A, A' (see fig. 2). On expanding, it raised the distance-piece and knife-edge fixed to the upper jaw, causing a rotation of the lever B about a pair of coplanar knife-edges at C. Vibration of the pointer was prevented by two light return-springs at D, while the body of the extensometer itself was held firmly inside the containing tube by the compression-springs E, E', E''.

The lever magnified the movement about 40 times, so that with the aid of a reading microscope an expansion of one two-thousandth of a millimetre could be detected with certainty. The interposition of the curved surface of the containing tube between the pointer and measuring instrument rendered necessary the application of an optical correction to each reading.

Perhaps because the return-springs were rather too light, the extensometer could not always be relied upon when a change occurred in the direction of movement (as, for example, when heating and cooling *in vacuo*). In consequence, the zero-point reading in each experiment was subject to a greater error than readings taken when the pointer was moving continuously in the direction of expansion.

This error could be estimated by carrying out series of experiments under precisely reproducible conditions; it never exceeds 4×10^{-3} mm.
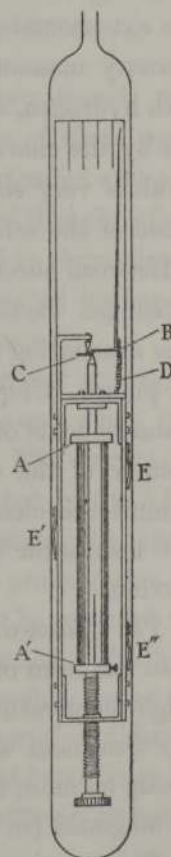

Fig. 2.

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The large deadspace of the extensometer vessel, a great portion of which was subject to the fluctuations of room temperature, rendered the adsorption values far more difficult to determine with accuracy. On account of the necessity for introducing successive and carefully controlled quantities of gas to the charcoal a method was adopted whereby the gas was generated, as required, from solid materials contained in a detachable weighing tube. This tube, or generator, which carried a tap, and in some cases also a phosphorus pentoxide tube, connected through a push-join with a capillary-tube system, from which other taps led on the one side to the sorption vessel and on the other to the drying train and pumps. Between each successive generation of gas the taps carried by the weighing tube and by the extensometer vessel were closed; dry air was admitted into the connecting capillary and the weighing tube detached and weighed. The unadsorbed residues of gas in the extensometer vessel and capillary system were estimated by means of a mercury manometer sealed to the former. The deadspaces were calibrated with hydrogen, an appropriate correction being applied for the sorption of this gas by the charcoal. An error in estimating this correction would affect the s-values very slightly in the case of carbon dioxide and quite inappreciably those of the other gases.

Between successive experiments the extensometer vessel was submitted to prolonged vacuum-heating at $220°$ C. in an electrically controlled furnace. The evacuating system comprised a condensation pump backed by a rotatory oil pump. Unquestionably the treatment did not suffice to remove the last traces of some of the gases, but the presence of the extensometer and the large volume of the containing tube rendered it both dangerous and difficult to submit the charcoal to more drastic treatment. The method of correcting the results for the presence of these small residues is described in the next section.

The Charcoal.—A piece of pre-war German willow charcoal was used, cut into the form of a rod $8 \times 0.8 \times 0.8$ cm. No means being available for its high-temperature treatment, no attempt was made to reduce its ash-content by treatment with acid. The ash-content was comparatively low, however, being no more than 0.9 per cent. The " block " density of the specimen was 0.30 grams per cubic centimetre.

The experimental gases were generated as follows :—

Ammonia.—The gas, after preparation and liquefaction, was fractionally distilled over solid potash and passed through phosphorus pentoxide into a tube containing carefully dried silver chloride. From the latter

it was driven, as required, into the weighing tube, which also contained silver chloride. The gas so treated was sufficiently dry to pass through a good phosphorus pentoxide tube without the latter becoming visibly affected.

Water Vapour.—From hydrated copper sulphate contained in the weighing tube.

Carbon Dioxide.—From sodium bicarbonate and phosphorus pentoxide; a phosphorus pentoxide tube was sealed to the weighed generator to prevent loss of water.

Sulphur Dioxide.—From normal sodium sulphite and phosphorus pentoxide; here also a phosphorus pentoxide drying tube was used.

Summary of Results at Room Temperature.

The reproducibility of the results with ammonia and sulphur dioxide was slightly interfered with by the presence of the small residues of these gases which resisted removal by the normal heat treatment. An extended series of experiments carried out with ammonia, however, clearly showed that the effect of these residues was slightly to displace the x, s curves parallel to themselves; the necessary zero-point corrections could, therefore, be estimated by superposing the graphs on those given by the uncontaminated charcoal.

The measurements with water vapour at low s-values showed a curious inconsistency which could not be ascribed to the same cause, since the irregularity disappeared when higher values were reached. The results of several sorption experiments with this substance are illustrated in fig. 3 by plotting x against $s/S - s$. According to the hyperbolic equation, the result should be a linear graph passing through the origin; since the prolongation of the line cuts the axis well above this point, water vapour must be regarded as exceptional, in that even the first traces cause a marked expansion. Further investigation of this interesting region was unfortunately impossible, owing to the very considerable errors involved in estimating small sorption values. Apart from this irregularity the s, x relations appear no different from those of the other gases, in spite of the near approach to saturation conditions, and the generally anomalous behaviour of water as an adsorbate.
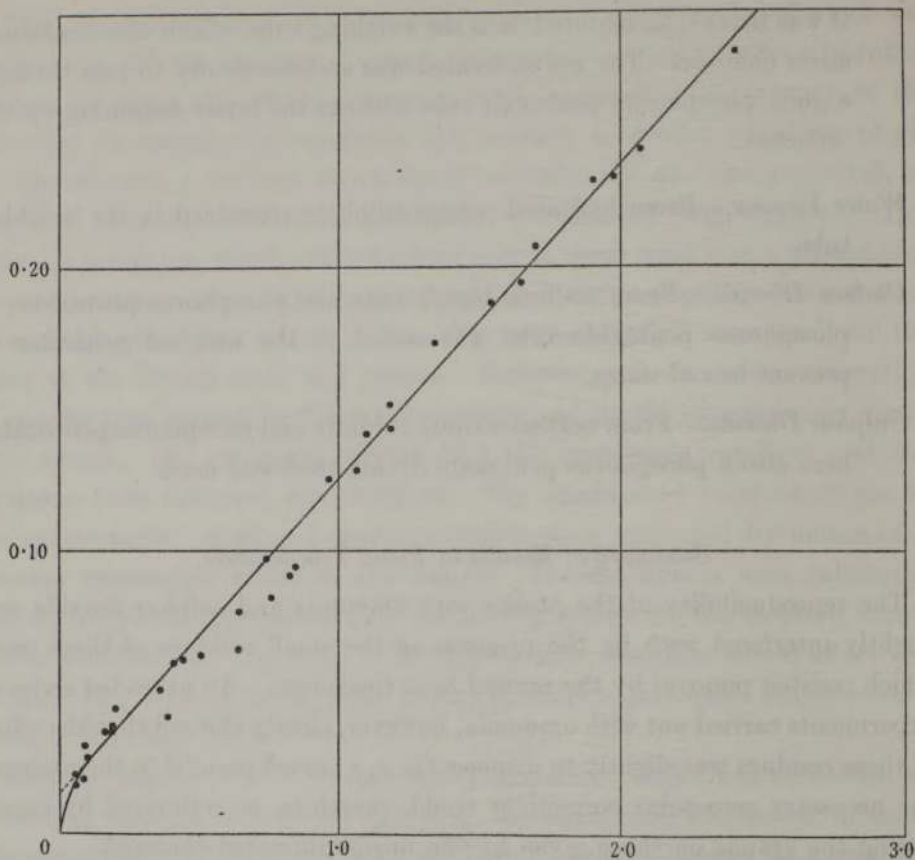
Fig. 3.—Water Vapour at 20°.   Abscissæ $s/(S - s)$.   Ordinates, x per cent.

The following table summarises the results of typical experiments with the four gases, and gives, for comparison, the x-values calculated from the hyperbolic equations.

Table II.

s = sorption value in grams per gram of charcoal.

x = linear expansion per cent. at room temperature (18° to 20° C.).

WATER. $S = 0 \cdot 158$ gram. $k = 0 \cdot 110$ per cent.					CARBON DIOXIDE. $S = 0 \cdot 139$ gram. $k = 0 \cdot 143$ per cent.			
s.	s/S.	x obs.	x calc.	Diff. $\times 10^3$.	s.	s/S.	x obs.	x calc.
0·0081	0·051	0·018	0·004	14	0·0136	0·098	0·016	0·015
0·0251	0·158	0·035	0·021	14	0·0294	0·213	0·038	0·038
0·0484	0·306	0·058	0·048	10	0·0506	0·364	0·081	0·081
0·0680	0·430	0·094	0·082	12	0·0582	0·419	0·102	0·103
0·0778	0·492	0·122	0·106	16	0·0647	0·465	0·123	0·124
0·0906	0·573	0·170	0·148	22	0·0676	0·486	0·137	0·135
0·1066	0·674	0·238	0·228	10	0·0729	0·524	0·158	0·157

AMMONIA. $S = 0 \cdot 112$ gram. $k = 0 \cdot 252$ per cent.				SULPHUR DIOXIDE. $S = 0 \cdot 210$ gram. $k = 0 \cdot 1705$ per cent.			
s.	s/S.	x obs.	x calc.	s.	s/S.	x obs.	x calc.
0·0099	0·089	0·026	0·025	0·0221	0·105	0·023	0·020
0·0165	0·148	0·042	0·044	0·0501	0·239	0·052	0·053
0·0227	0·202	0·064	0·064	0·0777	0·371	0·096	0·101
0·0378	0·337	0·128	0·128	0·1021	0·486	0·162	0·162
0·0455	0·406	0·171	0·172	0·1377	0·656	0·329	0·327
0·0512	0·458	0·212	0·212	0·1424	0·679	0·361	0·361
0·0611	0·546	0·303	0·303	0·1486	0·708	0·414	0·414
0·0653	0·583	0·354	0·353	0·1522	0·724	0·448	0·447
0·0706	0·631	0·427	0·428	0·1532	0·730	0·461	0·461

Discussion.

Considered in conjunction with the essentially anisotropic macro-structure of charcoal, the observation of Meehan that the expansion accompanying adsorption is equal in all directions provides sufficient evidence that adsorption is a process affecting the fine internal structure of the walls of the macropores, and not one concerned merely with their free surfaces. The effect of the macropores is thus to magnify the observed expansion of a given weight of charcoal in proportion to the " block " volume.

Of recent years much evidence has accumulated which suggests that molecules adsorbed on solids have, in many cases, freedom of movement in directions

parallel to the surface.*   Where the surface is plane or convex, this could hardly give rise to any distending effect, but it might well be that in the case of such a fine-structured solid as charcoal the adsorbed film exerts a wedge-like action resulting from molecular bombardment taking place at sharp re-entrant angles in the surface.   ·

With the rise of concentration at the free surface of the charcoal there would be a more than proportionate increase in the surface pressure, as the " incompressible " volume associated with the molecules approaches more and more closely the total space available for the adsorbed phase.†

The limiting sorption values S are to be distinguished from the saturation values found by direct measurement of the adsorption in contact with saturated vapours.   Further experiments with water vapour have indicated that the condition of saturation is reached without serious departure from the hyperbolic relationship.   That the S-values of the four substances examined represent nearly equal volumes of the normal liquids appears to signify that the total space available for the adsorbed phase (which, as saturation is approached, must approximate more closely to the normal liquid condition) is nearly equal in all four cases.   It does not, however, follow that the films are all of equal thickness, for possibly their area is considerably greater in the case of substances which have smaller molecules.

The Effect of Temperature : Experiments with Ammonia.

Since the experimental temperature, though nearly constant in any one experiment, varied somewhat from one run to another, it was of some importance to determine the influence of this factor on the expansion measurements. Four experiments were carried out with ammonia, covering the range from 0° to 75° C.   It was found that for any given value of s the corresponding x was slightly greater at higher temperatures.   So small was the variation, however,

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* See, for example, Volmer and Adhikari, ' Z. Physik,' vol. 35, p. 170 (1925) ; Volmer, ' Z. Physikal Chem.,' vol. 115, p. 255 (1925) ; Frenkel, *ibid.*, vol. 33, p. 366 (1925) ; ' Chem. Soc. Annual Reports,' vol. 25, p. 350 (1928), where further references are given.

† Schofield and Rideal, ' Proc. Roy. Soc.,' A, vol. 109, p. 57 (1925), propose, as the equation of state of molecules adsorbed at the surfaces of solutions, an equation

$$F \left(\frac{1}{\Gamma} - B \right) = i\, R\, T,$$

where F is the surface pressure, Γ the (excess) surface concentration, B a constant standing for the smallest area the (gram) molecule can occupy, and i a constant depending on the lateral cohesion between molecules.   The similarity of form between this and the empirical equation for the expansion is probably not without significance.

that these experiments yielded no indication as to whether the temperature changes had influence on one or on both of the constants k and S. If S be supposed constant (an assumption which finds some support from considerations dealt with in the last section), k is found to vary roughly in proportion to the absolute temperature, taking the following values at the temperatures stated :—

T (° absolute)	273	293	321	348
k (per cent.)	0·231	0·252	0·266	0·306

It should be remarked, however, that no high degree of accuracy is claimed for these measurements, which aimed primarily at assessing the errors introduced into the experiments previously described by the fluctuations of room temperature.

We are indebted to Dr. Stradling and Dr. Meehan for details of the extensometers used by them at the Building Research Laboratories, and also for adding to our stock of charcoal suitable for extensometric experiments.

Summary.

An apparatus is described by which the linear expansion of a charcoal rod can be measured simultaneously with the quantity of adsorbed gas causing it. The expansion (x) is found to be related to the adsorption value (s) by equations of the type

$$x = k \frac{s}{S - s}$$

where k and S are constants. The values of the latter constant for the four gases examined represent nearly equal volumes of the normal liquids at the experimental temperature. The hypothesis is advanced that the expansion results from the pressure exerted by the adsorbed molecules at sharp re-entrant angles in the surface of the adsorbent. The expansion caused by the adsorption of a given quantity of gas increases with the temperature.