

## DISCONTINUITIES IN ADSORPTION PROCESSES.

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About six years ago, workers in this laboratory first began to obtain evidence to the effect that the process of the adsorption of vapours on charcoal might be discontinuous in nature. The results were, for some considerable time, regarded with not unnatural suspicion, and every attempt was made to eliminate the errors to which they might be due. Such attempts were unsuccessful, and the real existence of these discontinuous phenomena is now regarded by us as proven. What follows is merely a summary of the evidence on which this conclusion is based.

## 1. Synopsis of Results already Published.

(a) **Experiments at Low Pressures of Vapour and in Absence of Air.**—The first observed discontinuities were noticed during these measurements, limited by the experimental method (use of the Pirani gauge) to maximum pressures of the order of 0.2–0.5 mm. They appeared in the isosteres of all  $\text{CCl}_4$ —charcoal systems, determined over temperature ranges varying between  $0^\circ$ – $90^\circ$ , whenever the  $\text{CCl}_4$  pressure exceeded about 0.1 mm., the molecular heat of adsorption, constant up to that pressure, undergoing a sudden diminution.<sup>1</sup> They were also observed at the same pressure in certain isothermals<sup>2</sup> measured at  $25^\circ$ , and indications were obtained of the existence of further breaks at higher pressures. The nature of these isothermal breaks is expressed by saying

<sup>1</sup> Allmand and Chaplin, *Proc. Roy. Soc.* **129A**, 257, 1930.

<sup>2</sup> Allmand and Chaplin, *loc. cit.*, p. 246; Allmand and Puttick, *ibid.*, **130**, 197, 1930.

that, as the pressure is increased and reaches a certain figure, the value of  $dq/dp$  abruptly increases, then decreasing continuously until the next discontinuity is reached. The general effect is to cause the appearance on the isothermal of sharply defined loops, concave to the pressure axis. Further work<sup>3</sup> showed that the isosteres for  $\text{CS}_2$  on a whole series of charcoals, determined over the same temperature range, also exhibited discontinuities at pressures of 0.1 mm. or a little higher. One carefully studied isothermal showed the same phenomenon.

**(b) Experiments in Presence of Air, using the Retentivity Technique.**—This method of obtaining approximate sorption isothermals, originally devised by Allmand, Manning and Burrage,<sup>4</sup> was developed later by Burrage<sup>5</sup> in such a way as to furnish true isothermals. A very large number of such isothermals have been measured<sup>6</sup> on a variety of charcoals, chiefly using water vapour or  $\text{CCl}_4$  as sorbates, and working either at 100° or at 25°. The invariable result has been a curve of markedly discontinuous structure, showing a first break at about 0.1 mm., independent of the nature of both charcoal and sorbate, and also of temperature, and showing, in addition, a large number of similar breaks at higher pressures, some of them well, some indistinctly, marked. Attempts to correlate satisfactorily either the pressure values at which breaks occurred, or the increments of sorbate between adjacent breaks, led to no particular success, although there was evidence of a certain degree of regularity in the pressure values.

**(c) Experiments at Moderate Pressures of Vapour and in Absence of Air.**—These measurements<sup>7</sup> were undertaken primarily to confirm the general nature of the results just described, obtained, as they were, by a new and untried technique, and also to provide a rather greater variety of experimental material. Apparatus and sorbent were thoroughly degassed before admission of the vapour, and equilibrium pressures were read off by a mercury manometer, taking measures to avoid false pressures due to displaced gases, and making readings at narrow pressure intervals in order better to define the anticipated breaks. As a result, it was found that every charcoal isothermal investigated, using as sorbates  $\text{CCl}_4$ ,  $\text{CS}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{H}_2\text{O}$ ,  $n\text{-C}_5\text{H}_{11}\text{OH}$  and  $\text{CO}_2$  (the latter above and below its critical temperature), exhibited breaks. In two cases of  $\text{CCl}_4$  isothermals, it could be shown that the broken curves were reversible in nature.

**(d) Experiments with Silica Gel.**—Isothermals<sup>6</sup> over a limited pressure range, determined by the approximate retentivity method, showed a very markedly discontinuous and step-like structure in the case of water vapour, and definite evidence of minor discontinuities with  $\text{CCl}_4$ . On the other hand, a benzene isothermal determined in absence of air appeared continuous within experimental error between 7.5–12 mm.

## 2. New Results.

**(e) Carbon Dioxide on Charcoal.**—The results mentioned under 1(c) as having been obtained with  $\text{CO}_2$  and charcoal were known not to represent equilibrium data, and would have been doubted if they had

<sup>3</sup> Allmand and Lizius, *Proc. Roy. Soc.*, **134A**, 554, 1932.

<sup>4</sup> *J. Soc. Chem. Ind.*, **47**, 369 T, 372 T, 1928.

<sup>5</sup> *J. Physic. Chem.*, **34**, 2202, 1930.

<sup>6</sup> Allmand and Burrage, *J. Physic. Chem.*, **35**, 1692, 1931.

<sup>7</sup> Allmand and Puttick, *loc. cit.*; Allmand and Burrage, *Proc. Roy. Soc.*, **130A**, 610, 1931.

stood alone. In addition to this, a  $\text{CO}_2$ -charcoal system is of rather particular interest, in view of the special rôle played by the slow displacement of this gas from a charcoal surface during adsorption measurements with other substances. Also a further test of the reproducibility of the breaks was thought desirable. Consequently, an isothermal has been examined<sup>8</sup> in great detail by the static method, about 350 points having been determined at  $25^\circ$  within the pressure range 81 — 0.04 mm., viz., 192 points covering the range 81 — 1.55 mm. (series I), then 37 points between 1.78 — 0.04 mm. (series II), followed by 90 points covering 16.80 — 1.60 mm. (series III), and finally 28 points ranging between 79.4 and 12.75 mm. (series IV). A complex discontinuous isothermal

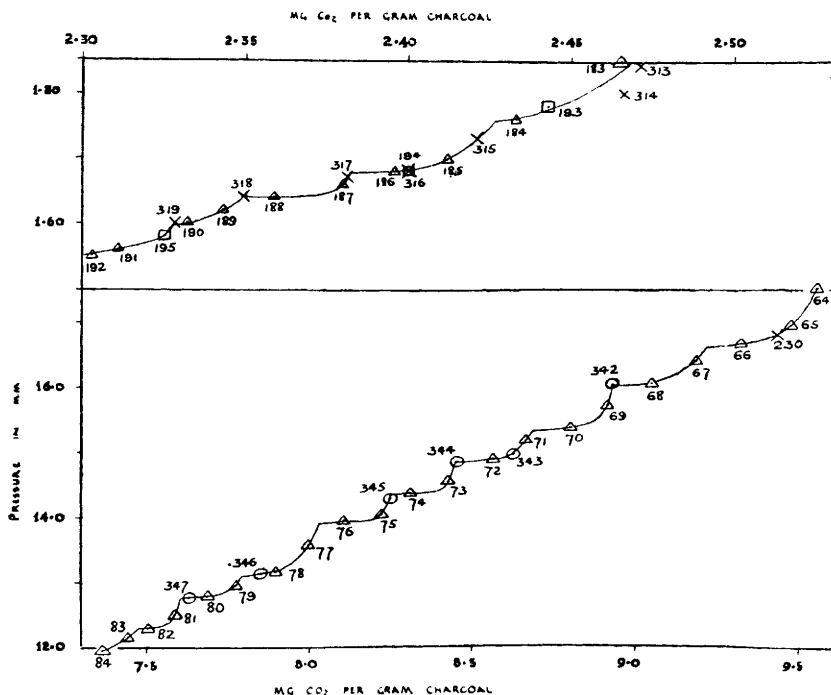


FIG. 1.

was obtained over the whole pressure range and, moreover, the different desorption curves were superposable in detail when their pressure ranges overlapped. Fig. 1 contains plotted data for the pressure intervals 1.55 — 1.85 mm. and 12.0 — 17.5 mm., involving respectively points determined during series I, II, III and I, III, IV. (I  $\Delta$ ; II  $\square$ ; III  $\times$ ; IV  $\circ$ .)

(f) **Various Vapours on Charcoal and on Silica Gel, Employing an Improved Retentivity Technique.**—These experiments<sup>9</sup> have furnished the very striking result that, in every case investigated, both with charcoals, activated and unactivated, and also with silica gel, the isothermals above 0.1 mm. appear to consist of sharply defined rectangular steps, with the treads, as drawn, parallel to the  $q$  axis. (Five different charcoals, and  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CCl}_4$  and  $\text{SO}_2$  have been worked with.)

<sup>8</sup>, <sup>9</sup> Burrage—unpublished work.

Such a structure had already been noticed with water and silica gel—see I(d),—and the fact that, with a more precise method of measurement, it is now generally obtained, is ascribed to the very effective displacement of residual gases and vapours brought about by the method of charging with the vapour under experiment. In the case of charcoals, it is the residual oxygen charge which is thus removed. It may be added that *sorption* isothermals, determined by charging in an air stream, also show a step-like structure.

One further important point has emerged, *viz.* that, using  $\text{CCl}_4$  at  $25^\circ$ , the quantity increments between successive breaks (given by the "treads" of the "steps") are practically constant within the experimental error, both with charcoal and with silica gel, over the whole pressure range covered in the experiments, *viz.* 8 — 0.1 mm. (See Fig. 2.) On the other hand, with water vapour, whilst these decrements are con-

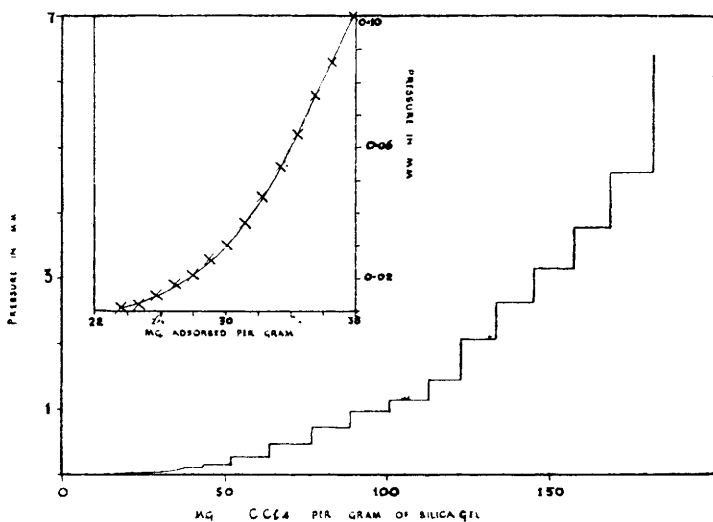


FIG. 2.

stant when starting at high pressures, they increase at intermediate pressures and finally fall off again as the pressure is progressively reduced. It is of interest to note that the absence of discontinuities below 0.1 mm. (provided that disturbing influences are not present) found in the earlier experiments, is confirmed.

(g) **Adsorption of Mixtures of Vapours on Charcoal.**—Experiments using the Pirani gauge low pressure technique<sup>10</sup> have shown that the adsorption of mixtures of the vapours of  $\text{CS}_2$  and  $\text{H}_2\text{O}$  by charcoals also may involve discontinuities. The work is difficult, and the relations are not too exactly defined. But it can be stated that the isothermals of  $\text{CS}_2$  on charcoals holding a constant charge of water show signs of discontinuities, and this is very decidedly the case when the effect of a variation in the water charge on the equilibrium  $\text{CS}_2$  pressures exerted by a constant charge of  $\text{CS}_2$  at constant temperature is considered; the  $p_{\text{CS}_2}/q_{\text{H}_2\text{O}}$  curves sometimes show very marked breaks.

<sup>10</sup> Allmand and Lizius—*unpublished work*.

(h) **Adsorption from Solution.**—Experiments<sup>11</sup> have been carried out on the adsorption of phenol from aqueous solution by an activated charcoal. The isothermals, both at 25° and at 60°, are of a marked step-like character, and are reversible, or very nearly so.

### 3. Other Similar Results.

A summary, up to the end of 1930, of observations from other laboratories indicating that adsorption processes may be discontinuous in nature, has been given elsewhere.<sup>12</sup> Since that date has appeared an important paper by Benton and White,<sup>13</sup> in which are given details of discontinuous hydrogen isothermals measured on reduced nickel, copper and iron catalysts, both bare and poisoned with CO, together with similar nitrogen isothermals on copper and iron. These authors in addition have put forward a theory which accounts very plausibly for a large number of the facts observed by them, and which has points in common with certain views which we held a few years back,<sup>14</sup> but which we have not been able to develop to our satisfaction in the interval, owing to the complexity of the available experimental data, and the wish to elucidate them more exactly. The analysis of the new results communicated in this paper is not completed, and fresh data are accumulating; on that account we shall not attempt here to elaborate further our preliminary views as already put forward<sup>15</sup>.

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<sup>11</sup> Chaplin (work carried out in the Research Laboratories of the Gas, Light, and Coke Company), *in course of publication*.

<sup>12</sup> Allmand and Burrage, *Proc. Roy. Soc.*, **130A**, 626, 1931.

<sup>13</sup> *J. Amer. Chem. Soc.*, **53**, 3301, 1931.

<sup>14</sup> The following is an extract from the printed report of a paper read by one of us in Oxford in December, 1929:—

The speaker finally briefly discussed possible explanations for the discontinuous structure of these isothermals which his experiments seemed to make probable. As a working hypothesis only (for there are difficulties and objections to be overcome and far more experimental work is needed) he inclined to the following. Adsorption on charcoal starts out from "active centres," from which "islands" of sorbate spread out, in the sense of Polanyi and Goldmann. An "island" is actually composed of a series of concentric rings. The completion of a ring and the commencement of a new one is marked by a "break." The spatial position of the rings with respect to the active centres is not invariable—they are closer in at high temperatures and with low-boiling sorbates than at low temperatures or with high-boiling sorbates. So Polanyi's "constant potential surfaces" (or lines) have no connection with the breaks.

<sup>15</sup> See preceding footnote; also Allmand and Burrage, *loc. cit.*, pp. 627 *et seq.*