365. *The Selective Adsorption of Heavy Water.*

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In a previous communication (J., 1934, 1207) preferential adsorption of heavier water by charcoal and silica gel was briefly reported. In our early experiments, as in the work of Washburn and Smith (*J. Chem. Physics*, 1933, **7**, 426), a quantity of the adsorbent was kept for some weeks in contact with a large volume of water, a procedure which, evidently, did not permit a speedy access of all the water to the adsorbent and hence was inefficient. Nevertheless, the results proved that an isotopic separation occurred, and the abnormally low density of the supernatant water after adsorption upon charcoal, when considered in relation to the moderate increase in density of the bulk of the desorbed water, indicated that the last traces of water held by the solid might be relatively very heavy. Therefore, the experiments now reported have been carried out by passing the vapour of tap-water over the adsorbent at 100° for a considerable time, these conditions being designed to facilitate the intimate contact of the whole of the water with the whole of the adsorbent. Silica gel and various samples of commercial charcoals gave increased densities for the desorbed water, estimated by the flotation method, which showed a fairly constant enrichment ratio markedly greater than that obtained by simple contact between the solid adsorbent and liquid water. As a check on these results, one adsorption was carried out upon pure charcoal with heavy water containing 4% of deuterium oxide. In this case, the concentration of deuterium oxide in the desorbed fractions was estimated by determinations of freezing point, and it was found that this method, which has not hitherto been applied, is both speedy and fairly precise.

EXPERIMENTAL.

Experiments with Commercial Adsorbents.—An iron tube, 125 cm. × 4 cm. inside diameter, wound with nichrome wire insulated by asbestos and heated electrically to a uniform temperature just above 100°, was used to contain the adsorbent. A measured volume of London tap-water was passed as steam through the tube. Then one end of the tube was closed and the other was connected to a pump *via* a cooled glass receiver and a manometer.

While the tube was maintained at 100°, successive fractions of the desorbed water were collected at successively lower pressures, each fraction being denoted by the pressure range in which it was collected.

The first experiment with 1 kg. of silica gel and about 8 l. of water gave the fractions labelled Ad. 4. A second similar experiment with 450 g. of active birch charcoal and 8 l. of water gave fractions Ad. 5. The third experiment (fractions Ad. 6) was made with the exceptionally active " Aron " rubber charcoal (160 g). and 8 l. of water. In a fourth experiment (fraction Ad. 7), with " acticarbone " (300 g.), 170 l. of water were used, and after the desorption at 100° was complete, the adsorbent was transferred to a silica tube and further fractions of desorbed water were collected at 200° (7·5%), 500° (0·75%), and 1000° (0·15%). These fractions proved to be too small for convenient measurement, but it is of interest that commercial charcoals do hold a small proportion of strongly bound water. In some cases this adsorption and desorption had to be repeated several times in order to obtain sufficient of the smaller fractions for determination.

Each fraction of desorbed water obtained by this procedure was rigorously purified by the methods previously described (*loc. cit.*), and its density determined to 0·2 γd by means of a silica float.

The results are in Table I, where our earlier results and those of Washburn and Smith are also given for comparison; T_S is the flotation temperature of the float in purified London tap-water, and T_{H_2O} the corresponding figure for the specimen of desorbed water. From these data it is possible to calculate the values given in the last two columns, showing respectively the concentration of deuterium oxide in the specimen and an " enrichment ratio," *i.e.*, the ratio of the final to the original concentration of deuterium oxide.

Experiment with Pure Charcoal.—It is well known that the adsorption of water on charcoal is influenced by impurities in the latter, by the presence or absence of an oxide film on its surface, and by the condition of that film if present (King and Lawson, *Trans. Faraday Soc.*, 1934, **30**, 1094). Therefore, in order to ascertain whether the impurities in the commercial adsorbents so far mentioned had affected the isotopic separation, it appeared desirable to carry out an experiment with pure charcoal under a rigorous vacuum technique. As the charcoal used (prepared by the method previously described; King and Lawson, *Kolloid Z.*, 1934, **69**, 21) was free from hydrogen, any possibility of interchange between water and hydrogen adsorbed on the surface was eliminated.

TABLE I.

Selective adsorption of D_2O *from water of normal isotopic concentration.*

Index No.	Pressure range of desorption, cm.	Total vol. of water desorbed at 100°, c.c.	% of total desorbed water in fraction.	T_s.	T_{H_2O}.	$(T_{H_2O}-T_s) \times 10^3$.	Δyd.	D_2O content, p.p.m.	Enrichment ratio.
Adsorption from steam.									
—	Standard		—	20·336°	20·336°	—	—	154	—
Silica gel.									
Ad. 4a	> 50	327	68	20·336	20·350	+ 14°	+ 2·9	189	1·23
Ad. 4b	< 50	—	32	20·336	20·362	+ 26	+ 5·5	219	1·42
Wood charcoal.									
Ad. 5a	> 60	191	19	20·336	20·349	+ 13	+ 2·7	186	1·21
Ad. 5b	60—40	—	20	20·336	20·349	+ 13	+ 2·7	186	1·21
Ad. 5c	40—20	—	35	20·336	20·350	+ 14	+ 2·9	189	1·23
Ad. 5d	< 20	—	26	20·336	20·361	+ 25	+ 5·3	216	1·40
Aron charcoal.									
Ad. 6a	> 40	160	38	20·344	20·357	+ 13	+ 2·7	186	1·21
Ad. 6b	40—20	—	39	20·344	20·365	+ 21	+ 4·4	205	1·36
Ad. 6c	< 20	—	23	20·344	20·370	+ 26	+ 5·5	219	1·42
" Acticarbone."									
Ad. 7a	> 40	241	36	20·347	20·361	+ 14	+ 2·9	189	1·23
Ad. 7b	40—20	—	42	20·347	20·368	+ 21	+ 4·4	205	1·36
Ad. 7c	< 20	—	22	20·347	20·373	+ 26	+ 5·5	219	1·42
Preliminary results.									
Ad. 2a	Supernatant water		—	20·336	20·334	− 2	− 0·4	149	0·97
Ad. 2b	Desorbed water		—	20·336	20·338	+ 2	+ 0·4	159	1·04
Ad. 3a	Supernatant water		—	20·336	20·332	− 4	− 0·8	144	0·94
Ad. 3b	Desorbed water		—	20·336	20·337	+ 1	+ 0·2	156	1·01
Results of Washburn & Smith.									
—	Standard		—	—	—	—	+ 53·0	790	—
—	Desorbed water		—	—	—	—	+ 46·5	712	0·90
—	Residual water		—	—	—	—	+ 59·7	870	1·10

Since it was not feasible in this experiment to employ the large quantities of material used in those already described, relatively heavy water was taken containing approximately 4% of deuterium oxide and changes in its concentration were observed by the freezing-point method described below.

Charcoal (4·6 g.), which had previously been activated by a short heating in oxygen at 400°, was heated to 1000° for 10 mins. in a closed crucible, cooled, transferred to a Pyrex bulb carrying a 2 mm. quill side tube, and thoroughly baked and out-gassed by heating to 400° for 18 hrs. at a pressure of 10^{-5} mm. Then pure water was distilled on to the charcoal at room temperature and left adsorbed in it for 3 days, the system being heated to 130° twice during this time, and finally the bulb was baked out and highly evacuated as before. This treatment was designed to remove the greater part of the oxide from the surface of the charcoal.

On to the charcoal thus prepared, 0·7 g. of water containing about 4% of deuterium oxide was distilled, and the apparatus was sealed off from the pump. After standing for 3 hrs. with a brief heating at 100°, the bulb was immersed in a steam-bath, and the end of the quill side tube was cooled, so that successive fractions of the desorbed water could be collected and sealed off in successive lengths of the tube. In each case an estimate was made of the relative humidity at which desorption occurred. The results are in Table II.

A small final fraction was collected at less than 4% relative humidity. Though it was too small (about 2 mg.) to permit a precise determination of the freezing point, a rough measurement indicated that the content of deuterium oxide was between 5·5 and 9%.

Estimation of Heavy Water Concentration by Determination of Freezing Point.—This method appears to be new, and has proved in the present investigation to be fairly accurate and speedy. It is, moreover, the only method which can be used with specimens weighing only a few mg.

It depends on the fact that a mixture of ice and water changes considerably in volume as melting or freezing proceeds, and remains constant in volume when held exactly at the f. p. In practice it is difficult to attain the latter condition, but we have found that under suitable conditions, when the tube containing the ice–water mixture is immersed in a bath kept at a steady temperature very close to the f. p. by immersion in a thermostat, the rate of expansion or contraction of the water–ice mixture is proportional to the difference between the bath temperature and the f. p. Thus, by means of several observations which bracket it, the f. p. can be quite accurately determined. The sealed tube containing a fraction of the desorbed water was fixed in contact with the bulb of a Beckmann thermometer immersed in the bath but isolated therefrom by a surrounding glass tube closed at the lower end. The bath contained dilute salt solution with ice on the surface and at the bottom, so that the middle layer of the bath would warm up gradually when undisturbed and could be kept at a constant temperature or cooled, when necessary, by bubbling a controlled current of air through the bath so as to mix in the cooler layers above and below. The presence of ice crystals does not interfere with the observation of the movement of the meniscus.

TABLE II.

Selective desorption of D_2O *from pure charcoal.*

Relative humidity.	Fraction of total adsorbed water, %.	M. p. (in vacuum).	D_2O, %.
Normal water	—	+ 0·007°	0·02
66—42	23	0·130	3·2
42—34	42	0·165	4·1
34—32	19	0·175	4·4
32— 4	16	0·190	4·8

In illustration of the conditions employed, it may be recorded that at the beginning of a determination the bath temperature was usually about 0·1° below the f. p. and rose during the measurement to within about 0·01° of the f. p., at which the rate of movement of the meniscus would be about 0·005 mm./min. The quantity of water necessary for a measurement is about 40 mg., in a 2-mm. tube, and the error of the mean of two or three sets of readings will not exceed about ± 0·005°. It is important to note that the presence of more than a small trace of air in the tube renders the method quite useless, as it may cause a spurious change in the f. p. of as much as 0·1°.

DISCUSSION.

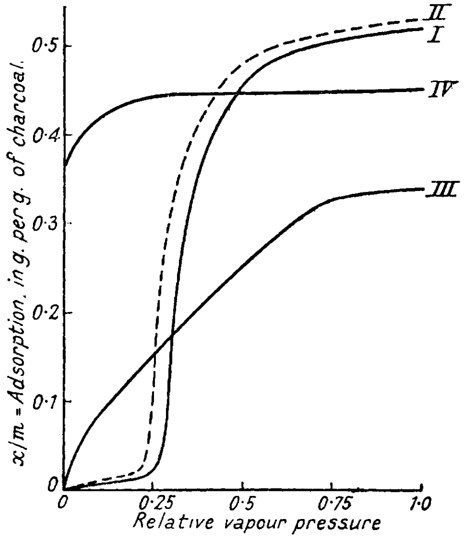
The results now obatined show that the adsorption of heavy water by charcoal and silica gel is markedly selective. When the adsorbent is merely left in contact with tap-water or other dilute solutions of heavy water, as in our preliminary experiments and in those of Washburn and Smith, a small concentration of the heavy water is observed, corresponding to an enrichment ratio of about 1·04—1·01. This method is obviously inefficient, for the only means of circulation is by diffusion, and the attainment of equilibrium must be extremely slow.

A much more effective method of examining the behaviour of mixtures is to adsorb them from the vapour phase : by this means the access of molecules to the whole surface of the adsorbent is greatly facilitated, and thorough and continuous admixture of the components in the vapour phase is secured. As " acticarbone," which had been treated with 20 times as much steam as the other adsorbents, gave the same separation as they did, it seems very probable that the degree of selective adsorption now observed represents the true equilibrium condition on the surface.

When, after this equilibrium is attained, the water is progressively desorbed, it is not constant in composition : the heavy water is preferentially retained (or, better, light water is preferentially evolved), and the last fractions of water removed from the adsorbent are relatively very heavy.

The relative enrichment by selective adsorption from steam was the same for silica gel and for three different kinds of charcoal, the density of the last fraction being the same in each case. Since, at the same time, the quantity of water desorbed varied with the activity of the charcoals, it appears that, as regards the charcoal–water system, the only effect of activation is to enlarge the area available for adsorption. This view is supported by the experiment with pure charcoal and more concentrated heavy water, where the first desorbed fraction contained 3·2% and the last main fraction 4·8% of deuterium oxide.

A good deal of attention has been given to the sorption of mixtures, and the recorded data show that, although selective adsorption is most marked when two different types of adsorption linkage are involved (*e.g.*, in the case of air on charcoal at ordinary temperatures or above, when oxygen is chemisorbed while nitrogen is held only by weak van der Waals forces), yet it undoubtedly occurs to some extent in nearly every system. Thus, for example, Dewar found (*Proc. Roy. Inst.*, 1906, **18**, 440) that charcoal exposed to a current of air at — 185° adsorbed 3 vols. of oxygen and 2 vols. of nitrogen, although at this temperature both gases are believed to be held physically. Moreover, on warming 50 g. of charcoal which had adsorbed 6 l. of air, the first litre of desorbed gas contained 18·5% of oxygen, the second 30·6%, the third 53%, the fourth 72%, and the fifth 80%. Again, Richardson and Woodhouse (*J. Amer. Chem. Soc.*, 1923, **45**, 2647), using mixtures of carbon dioxide and nitrous oxide in equal volumes adsorbed on charcoal, found that at 2870 mm. pressure only 57·3 c.c. of carbon dioxide were adsorbed for each 60·2 c.c. of nitrous oxide; and that on lowering the pressure, the disproportion increased until at 100 mm. pressure the adsorbed gas is two-thirds nitrous oxide.



In the system now under discussion it is interesting, therefore, to observe another case of markedly selective adsorption with two molecules of identical type, between which the chief difference is but a small fraction of the molecular weight. It seems not improbable, in such a case, that separation is largely influenced by some factor or factors other than zero-point energy differences.

In this connexion it should be noted that Lennard-Jones and Strachan (*Proc. Roy. Soc.*, 1935, *A*, **150**, 442) have worked out a wave-mechanical calculation of isotopic separation independent of the concept of zero-point energy. For the simple case of H_2, HD, and D_2 molecules adsorbed on copper at low temperatures, they show that the average times spent by HD and D_2 molecules on the surface are respectively 6 and 20 times that spent by H_2.

The adsorption of water on gas-free charcoal differs from the adsorption of other vapours in that there is practically no sorption at relative pressures below 0·3. At or above this pressure the adsorption rises suddenly to a relatively high value which increases but slightly with further increase in the relative pressure of water vapour. McBain, Porter, and Sessions (*J. Amer. Chem. Soc.*, 1933, **55**, 2294) explain the occurrence of this critical pressure by the assumption that it marks the stage at which the water molecules are held in the surface by mutual polarisation, whereas at lower relative pressures the chance of two water molecules alighting on adjacent points of the surface is small and so their mutual effect is negligible. The figure shows the isotherm of water on charcoal (I) and, for comparison, the isotherms of water on silica gel (III) and of a typical vapour on charcoal (IV). Now, the polarisability of the heavy water molecule is greater than that of ordinary water molecules, as is indicated, *e.g.*, by the relatively high temperature of maximum density for heavy water. Hence, upon the theory indicated above, it would be anticipated that, in the adsorption of heavy water on charcoal, the critical point should lie at a lower relative pressure than with ordinary water, as is indicated by the dotted curve (II) in the figure. The initial part of the curve for D_2O cannot be predicted but probably lies close to that for H_2O. A measurement of this isotherm will shortly be made in this laboratory. It seems possible that the difference in the polarisability of the two molecules may be the chief factor in the observed enrichment by adsorption, since this occurs to a marked extent at low relative pressures.

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