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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

## The Sorption of Vapors by Activated, Highly Evacuated, Sugar Charcoal Over Long Periods of Time<sup>1</sup>

BY JAMES W. MCBAIN AND R. F. SESSIONS

It is of great interest to observe the effects of long periods of time upon the sorption of vapors by charcoal. Previous experiments with the sorption balance have been observed over periods of a few hours or days but at no time for longer than one and a half months. This communication describes experiments<sup>2</sup> with ten vapors and one sample of activated sugar charcoal extending over a period of four to five years. The McBain-Bakr sorption balance affords the opportunity of keeping a sorption system sealed up for an indefinite period, while from time to time determining any desired equilibrium or other effect.

### Experimental

Kahlbaum pure sugar charcoal was used in all experiments. This charcoal was activated by heating in a fused silica crucible to red heat for several hours and finally for twelve hours in a fused silica tube placed in an electric furnace at approximately 1000°. During the latter heating a slow current of air was passed through the tube. The charcoal was then allowed to cool slowly in the

furnace, the air current being discontinued, and was poured into a glass stoppered bottle and shaken thoroughly. The activity of the charcoal thus treated was 27% (in 1930 and also in 1933) as determined by the amount of iodine which one gram of dried 200-mesh carbon sorbed from 50 cc. of a 0.2 *N* aqueous solution of iodine in 0.27 *N* potassium iodide.<sup>3</sup> This charcoal contained 0.0% ash.

Unusual care and precautions were taken thoroughly to cleanse the charcoal by heat and evacuation,<sup>4</sup> and during this process the liquid to be used remained within two sealed bulbs in the sorption tube. One bulb was broken open after the first drastic heating and evacuation, thus exposing the evacuated charcoal to the vapor.<sup>5</sup> Then after

(3) Method of N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, **15**, 1248 (1923). The activity may have been twice as great when the charcoal was activated in 1927; compare page 3.

(4) The buckets containing the charcoal were fitted with thin platinum foil covers, pierced with fine holes, to prevent the charcoal from blowing out during evacuation.

(5) After completion of the experiments, however, it was realized that a possible error in the technique of filling the sorption bulbs with liquid had been overlooked and that a minute quantity of air may in certain cases have been sealed into the bulbs with the liquid. The trace of air thus introduced, if any, is of course only a negligible fraction of the amount of gaseous impurities removed from the charcoal during its second evacuation after previous prolonged evacuation (five to nineteen hours at 600°) followed by cleansing. This second evacuation lasted from 73 to 414 hours at 600° and 10<sup>-5</sup> mm. This casts doubt upon the value of sorption experiments in which only one evacuation is performed. The technique of evacuation was sufficiently varied to affect the amounts of sorption so that the data here recorded are not intended for accurate comparison with each other. It may be pointed out that this washing process may be so conducted as to constitute an activation or, in some cases, a deactivation of the charcoal.

(1) Read in preliminary form at the Cincinnati meeting of the American Chemical Society, September, 1930.

(2) Method used by J. W. McBain, H. P. Lucas and P. F. Chapman [THIS JOURNAL, **52**, 2668 (1930)] with now the additional precaution of allowing time for cleansing vapor to permeate the charcoal. Similar precautions were found necessary by Harned [*ibid.*, **42**, 383 (1920)] to obtain reproducible rate of sorption. For other references to results with the sorption balance see J. W. McBain, "The Sorption of Gases and Vapours by Solids," George Routledge and Sons, Ltd., London, 1932, p. 128.

the final prolonged heating and evacuation and after the main tube had been sealed, the second bulb was broken.

The amount of sorption was determined by measuring the increase in length of the silica spring by means of a Wilson traveling microscope reading to  $\pm 0.01$  mm. The sensitivities of the springs lay between 89.5 and 204.7 mm. per gram; and from 0.0719 to 0.2355 g. of charcoal was used. Temperatures of the de Khotinsky air oven ( $T_1$ ), surrounding the upper half of the sorption tube, and of the paraffin oil bath ( $T_2$ ), in which the lower half of the tube was immersed, were determined by mercury thermometers which had been calibrated against a Bureau of Standards thermometer.

In Figs. 1-4 values for  $x/m$  are plotted against relative humidities,  $p/p_s$ ,  $p$  being the vapor pressure of the liquid at  $T_2$  and  $p_s$  the saturation pressure at the temperature of the isotherm,  $T_1$ . The vapor pressures were calculated by Dühring's rule, using data obtained from "International Critical Tables."<sup>6</sup> In all cases the measurements after four years were made by Miss Margaret McDowell.

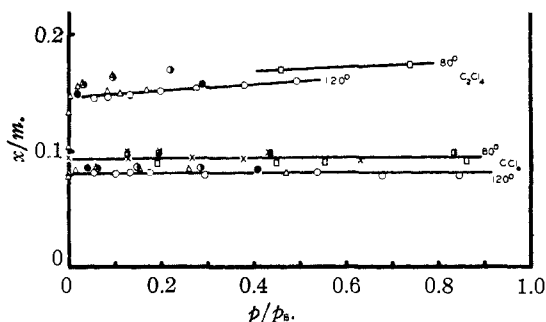


Fig. 1.—Carbon dichloride and carbon tetrachloride.  $\circ$ , sorption,  $120^\circ$ ;  $\triangle$ , desorption,  $120^\circ$ ;  $\square$ , sorption,  $80^\circ$ ;  $\times$ , desorption,  $80^\circ$ ; 23-46 days for carbon dichloride, 27-72 days for carbon tetrachloride.  $\bullet$ , sorption,  $120^\circ$ ; 2.8 years for carbon dichloride, 3 years for carbon tetrachloride.  $\circ$ , sorption,  $120^\circ$ ;  $\blacktriangle$ , desorption,  $120^\circ$ ;  $\blacksquare$ , sorption,  $80^\circ$ ;  $\blacktriangleright$ , desorption,  $80^\circ$ ; 4.6 years (by M. McD.).

A point not brought out by suppressing the numerical data and presenting them only in graphical form is that the readings further to the left on each graph were taken with the lower temperature at  $-186^\circ$  except in the case of the two amines. This illustrates the extent to which sorption goes at infinitesimal pressures with dras-

(6) Data only for boiling point and critical temperature were available for pyridine. For triethylamine the vapor pressure data of R. T. Lattay [*J. Chem. Soc.*, **91**, 1971 (1907)] were used.

tically cleaned charcoal in a sealed system. It will be noted that the pressures used extend up to the vapor pressures of these volatile liquids at temperatures up to  $113^\circ$  for butyric acid and carbon tetrachloride,  $103^\circ$  for chloroform, and  $96^\circ$  for carbon disulfide, carbon dichloride, pyridine, triethylamine and diethylamine.

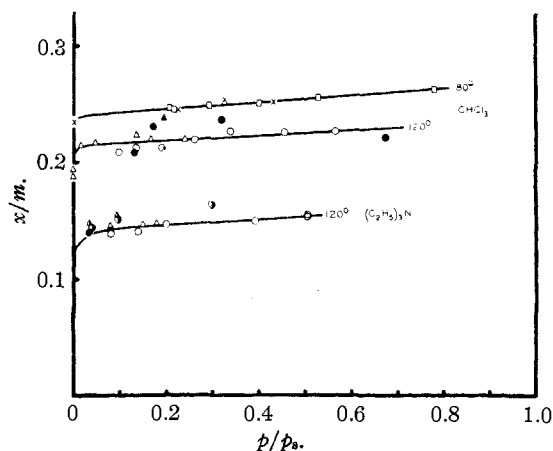


Fig. 2.—Chloroform and triethylamine.  $\circ$ , sorption,  $120^\circ$ ;  $\triangle$ , desorption,  $120^\circ$ ;  $\square$ , sorption,  $80^\circ$ ;  $\times$ , desorption,  $80^\circ$ ; 34-62 days for chloroform, 24 days for triethylamine.  $\bullet$ , sorption,  $120^\circ$ ;  $\blacktriangle$ , desorption,  $120^\circ$ ; 2.3 years for chloroform, 2.8 years for triethylamine.  $\circ$ , sorption,  $120^\circ$ ;  $\blacktriangle$ , desorption,  $120^\circ$ ; 4.6 years (by M. McD.).

### Discussion

The data here presented are unusual with regard to the drastic precautions taken to eliminate the impurities through rigorous evacuation of the charcoal, and unique in that they record the behavior of sealed up systems over a period of years.

Reversible equilibria are very rapidly attained over the whole range of pressures and temperatures, sorption and desorption leading to the same result. These experiments may be repeated indefinitely and in any order, the systems remaining sealed.<sup>7</sup> Miss McDowell, in our laboratory, has studied some of these sealed tubes in greater detail and has found that with pyridine the final adjustment of equilibrium under any new conditions is established to a high degree of precision within an hour, whereas with certain others, such as butyric acid, a detectable change extends over many hours. In addition to the data given in the figures, similar experiments were carried

(7) The reversibility is especially interesting in the case of carbon tetrachloride where the isotherms are so nearly independent of pressure but respond immediately to every change of temperature of the charcoal.

out with toluene and acetic acid up to periods of as much as four and a half and five years, respectively, the final readings being made by Miss McDowell who found them to lie within 4% of the original ones.

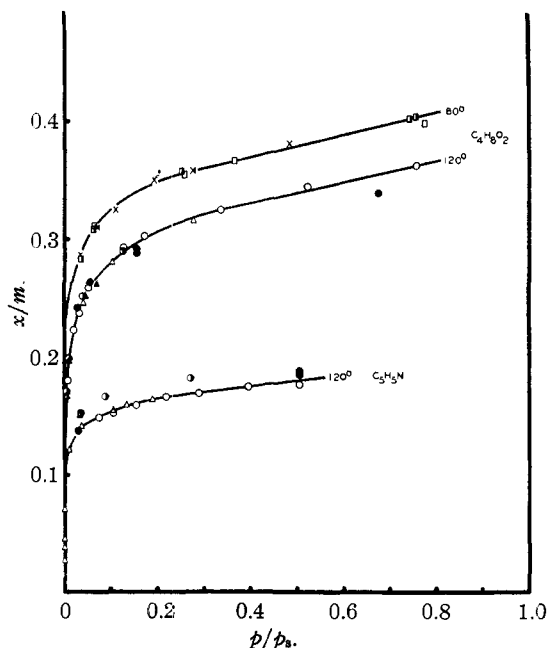


Fig. 3.—Butyric acid and pyridine.  $\circ$ , sorption,  $120^{\circ}$ ;  $\triangle$ , desorption,  $120^{\circ}$ ;  $\square$ , sorption,  $80^{\circ}$ ;  $\times$ , desorption,  $80^{\circ}$ ; 46–93 days for butyric acid, 25–32 days for pyridine.  $\bullet$ , sorption,  $120^{\circ}$ ;  $\blacktriangle$ , desorption,  $120^{\circ}$ ; 2.5 years for butyric acid, 3 years for pyridine.  $\ominus$ , sorption,  $120^{\circ}$ ;  $\blacktriangleleft$ , desorption,  $120^{\circ}$ ;  $\blacksquare$ , sorption,  $80^{\circ}$ ;  $\blacktriangleright$ , desorption,  $80^{\circ}$ ; 4.7 years (by M. McD.).

In the initial exposure of the charcoal to the vapor, equilibrium was attained in one or more days, in a few cases a week. Thereafter the equilibria remain almost constant throughout as much as four or five years, and presumably for an indefinite period.

This behavior is very different from that of charcoal exposed to vapors in the presence of impurities such as air, where the sorption is changing by several fold over a period of one or many months.<sup>8</sup> Solutions are still more different, for as McBain, and Firth, have shown, sorption increases one or more fold over a period of many years. This is clearly due to the difficult displacement of molecules of solvent by molecules of solute in interstices of molecular dimensions.

The fact that sorption is nearly complete at infinitesimal pressures is conclusive proof that the

(8) Compare J. Driver and J. B. Firth, *J. Chem. Soc.*, **121**, 2409 (1922).

vapors here studied are not taken up by capillary condensation in pores.

The isotherms differ very greatly from the classical formula for an isotherm, but all the data here presented, like those in previous communications with our adequately evacuated charcoal, follow the Langmuir sorption isotherm,  $x/m = abp/(1 + ap)$ , where  $a$  and  $b$  are empirical constants. This is shown by the straight line resulting when  $(p/p_s)/(x/m)$  is plotted against  $p/p_s$ . This relation cannot be tested for carbon tetrachloride since the variation over the range studied was negligible.

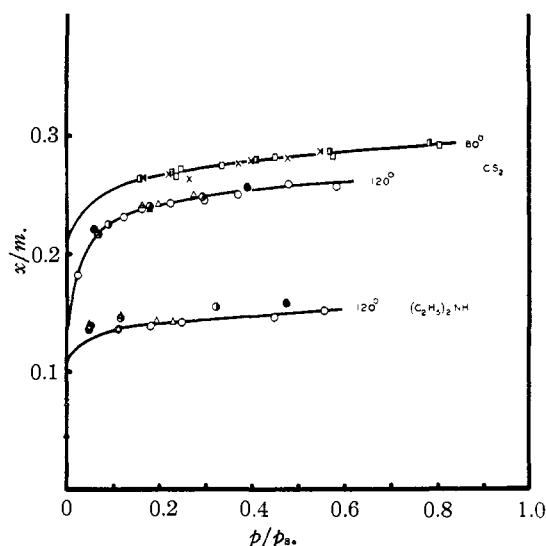


Fig. 4.—Carbon disulfide and diethylamine.  $\circ$ , sorption,  $120^{\circ}$ ;  $\triangle$ , desorption,  $120^{\circ}$ ;  $\square$ , sorption,  $80^{\circ}$ ;  $\times$ , desorption,  $80^{\circ}$ ; 19–48 days for carbon disulfide, 15 days for diethylamine.  $\bullet$ , sorption,  $120^{\circ}$ ;  $\blacktriangle$ , desorption,  $120^{\circ}$ ; 2.8 years.  $\ominus$ , sorption,  $120^{\circ}$ ;  $\blacktriangleleft$ , desorption,  $120^{\circ}$ ;  $\blacksquare$ , sorption,  $80^{\circ}$ ;  $\blacktriangleright$ , desorption,  $80^{\circ}$ ; 5 years for carbon disulfide, 4.6 years for diethylamine (by M. McD.).

It is very interesting to contrast the constancy of the sorptive power of the charcoal just described with its change on merely keeping a sample of the original charcoal in a stoppered bottle. In the one case it is preserved constant by being sealed up with saturated vapor. Unused samples, however, lost from 30–60% of their activity during the first year or two, but then remained nearly constant for the next few years.<sup>8,9</sup>

### Summary

Once more it is shown that adequate evacuation of charcoal leads to isotherms of highly dis-

(9) The results, with sugar charcoal and also redwood charcoal. (by R. F. S.) will be included in a further communication. Compare the similar deterioration of active charcoal kept in air observed by J. B. Firth [*J. Chem. Soc.*, **119**, 929 (1921)].

tinctive character, sorption being nearly completed at infinitesimal pressures.

Equilibria are fully established with great rapidity and thereafter remain constant and unchanged within a few per cent. for periods of many years provided the system is kept sealed.

On the other hand, if this charcoal, not exposed to vapor, is merely kept in a stoppered bottle, it loses a large percentage of its activity as determined by sorption of iodine (without previous treatment).

STANFORD UNIV., CALIF.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

## The Influence of Concentration on the Compressions of Aqueous Solutions of Certain Sulfates and a Note on the Representation of the Compressions of Aqueous Solutions as a Function of Pressure<sup>1</sup>

BY R. E. GIBSON

Experimental measurements of the effect of hydrostatic pressure on the volumes of solutions of different concentrations form an essential part of the data necessary for the calculation of the effect of pressure on the chemical potentials of the components and hence on phase equilibria involving these solutions. Three systems have already been studied,<sup>2</sup> and details concerning the determination of the experimental data and the computations have been described.

The apparatus for the determination of the compressions of solutions by the piston-displacement method<sup>2a,3</sup> at high pressures is not well adapted to measurements at low pressures, *i. e.*, up to 1000 bars. As the compressibility of all liquids diminishes rapidly with pressure, the relative volume change produced by the first thousand bars is extremely large, often being one-fifth to one-quarter of the total volume change produced by ten thousand bars, and should therefore be measured with as great precision as possible. The work described in this paper was undertaken to supply data on the compressions of solutions of different concentrations produced by a rise of pressure from atmospheric to one thousand bars, and at the same time to make as wide a survey as possible of the general effect of the nature and concentration of the solute on the compressions of aqueous solutions.

It is steadily being realized that any theory likely to be of useful application to actual solutions must account for all the properties of these

solutions not only under average laboratory conditions but also over any desired range of temperature and pressure. Furthermore, it is becoming apparent that in a complicated system such as an aqueous salt solution specific effects or effects characteristic of the chemical nature of the solute play a large part in determining the observed behavior of the solution. The importance of such effects may best be estimated empirically by the study of as wide a variety of substances as possible. From these points of view I shall discuss the regularities exhibited in the behavior of twelve sulfate solutions under pressure.

### Experimental

The apparatus for measuring the compressions of the solutions is shown diagrammatically in Fig. 1. The pressure was generated by forcing oil from a Tammann press into heavy-walled cylinders or bombs of vanadium steel, and was measured by an electrical resistance gage. During an experiment the bombs were immersed in a well-stirred thermostat maintained at  $25 \pm 0.02^\circ$ . Pyrex glass piezometers of capacities between 10 and 14 cc. were used for measuring the volume changes of the solutions. These piezometers differed only in size from those already described by Adams,<sup>4</sup> who has also described in detail the experimental technique, and the methods of computing the compressions from the observed quantities. The results in this paper are all based on the known compressions of Pyrex glass and mercury, which were taken as 0.00303 and 0.00399, respectively, at 1000 bars.

Several precautions, necessary if results reproducible within the precision of the pressure measurements are to be obtained, may be emphasized here. It is essential to prevent any permanent drop in the temperature of the liquid in the piezometer after the mouth of the reëntrant tube is sealed with mercury. Errors due to the formation of air bubbles while the solution is coming to the temperature of the thermostat may be eliminated by preparing the solutions from boiled distilled water and storing them prior to

(1) The substance of this paper was presented at the Washington Meeting of the American Chemical Society, March, 1933.

(2) (a) Adams, *THIS JOURNAL*, **53**, 3769 (1931); (b) Adams, *ibid.*, **54**, 2229 (1932); (c) Adams and Gibson, *ibid.*, **54**, 4520 (1932).

(3) Adams, Williamson and Johnston, *ibid.*, **41**, 12 (1919); Parsons and Cook, *Proc. Roy. Soc. (London)*, **85**, 332-349 (1911); Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 1 (1913).

(4) Adams, Ref. 2a, pp. 3773-3776.