shortened the time in Expt. 2 with 0.95 mg. of potassium by 15 minutes, and in Expt. 4 with 0.48 mg. of potassium, two hours were saved.

In Expts. 4 and 5 containing 0.48 mg. and 0.3 mg. of potassium, respectively, the test for potassium in the filtrate (not removed by zirconium sulfate) was very faint and appeared only after allowing the test to stand for forty minutes.

Summary and Conclusions

1. "Seeding" by adding a solute dispersoid furnishes suitable nuclei for initiation of visible precipitation without introducing appreciable quantities of the material to be detected.
2. The addition of a drop of a dispersoid of the desired product hastens the detection of potassium by zirconium sulfate.
3. The sensitivity of zirconium sulfate reagent for potassium was increased through the presence of the dispersoid from 0.48 mg. of potassium to 0.32 mg. per 2 cc. of reaction mixture.
4. The zirconium sulfate reagent did not completely remove potassium from solution.

Columbus, Ohio

THE SORPTION OF ORGANIC VAPORS BY HIGHLY EVACUATED, ACTIVATED SUGAR CHARCOAL[1]

By James W. McBain, H. P. Lucas and P. F. Chapman

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It is of the greatest interest to determine in how far sorption data for a given specimen of charcoal may be made reproducible through improvements in the preliminary treatment, and then to ascertain in how far differently activated specimens of the same charcoal yield sorption data conforming to a definite type. In previous communications,[2] it has been increasingly shown that improvements in the preliminary evacuation of a given specimen of charcoal greatly affect not merely the position, but also the form of the sorption curve. This becomes especially noticeable as the cleansing of the charcoal through evacuation is made very thorough. It is found advisable to evacuate for a long period at as high a temperature as possible in a high vacuum, then to displace some of the impurities still sorbed on the charcoal by admitting to the charcoal some of the liquid to be investigated and repeating the thorough evacuation before commencing the experiment.

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[1] These experiments were carried out at the University of Bristol, England, in 1925–1927 inclusive.

[2] A. M. Bakr and J. E. King, *J. Chem. Soc.*, **119**, 454 (1921); A. M. Bakr and J. W. McBain, This Journal, **46**, 2718 (1924); J. W. McBain, *Nature*, **117**, 550 (1926); J. W. McBain and G. T. Britton, This Journal, **52**, 2198 (1930); J. W. McBain, D. N. Jackman, A. M. Bakr and H. G. Smith, *J. Phys. Chem.*, **34** (1930).

This communication describes experiments with seven organic chemicals, using four air and steam activated charcoals made from the same pure sugar charcoal.[3] Definite regularities have been found, and it is shown that some specimens of charcoal possess a saturation value in that they sorb as much vapor at low as at high pressures, whereas other specimens exhibit sorption which definitely rises even in the higher ranges of pressure.

A sorption balance, such as that of McBain and Bakr,[4] used in a tube which remains sealed throughout the course of the experiments, proved highly advantageous for the study of these differential effects.

Experimental

The liquids were Kahlbaum's best and were redistilled before use. Four charcoals prepared from the same sugar charcoal were employed and are designated as follows.

"Air and Vacuum B."[5]—Prepared by A. M. Bakr in 1923 by heating *in vacuo* in a silica flask for fifty-six hours in the tip of the blowpipe flame, admitting a very slow current of air during the first six hours.

"Air C."[5]—Prepared by H. G. Smith in 1925 by heating for twelve hours in an unglazed porcelain tube at 1140° (measured), a slow current of air being passed throughout and burning away 20% of the charcoal.

"Steam D."[5]—Activated in 1925 by H. H. M. Wright by heating in a silica flask at 700° for forty-five minutes in a current of steam and continued heating for ten minutes.

"Steam E."—Activated by Chapman in 1927 by heating in a silica flask at 650° (measured) for thirty minutes and then blowing a current of steam directly on the charcoal for forty-five minutes during which the flask was shaken, the temperature falling to 600°; the charcoal was heated for ten minutes further and on cooling resembled a fluid.

It was found that springs of fused silica increase in length when heated under load, although the elastic constant is far less affected. No change can be detected during six weeks at 40°, and the change at higher temperatures rapidly diminishes as heating is continued.[6] These effects are readily obviated by heating the spring under load at 300° for two days before calibration. Recalibration at the end of an experiment shows this to be effective. The initial increase of the length of a spring under a load of 0.26 g. is about 0.0028 cm. per hour at 440°.

About 0.1 g. of charcoal was used in a bucket of gold foil weighing less than 0.1 g. It was found by blank experiments that the weight of vapor sorbed by the gold bucket was far less than the number of figures to which the weight of vapor sorbed by charcoal was read.[7]

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[3] For analyses and tests see previous communications.

[4] J. W. McBain and A. M. Bakr, THIS JOURNAL, **48**, 690 (1926).

[5] See previous communications for other measurements with this charcoal. The conditions of activation were not ideal and do not afford a legitimate comparison between the possibilities of air and steam activation; for example, in the latter case the temperature was too low.

[6] The physical properties of fused silica are well known to be undefined (Footnote 7 of Ref. 2). We have on several occasions had a spring break when carrying less than a previous load, and, on one occasion, we have seen a spring rather suddenly change its length and sensitivity.

[7] Using a gold bucket of 22.6 sq. cm. area and a spring extending 0.694 mm. per milligram at 120°, extension was not definitely noticeable until the vapor pressure of toluene was 250 mm., and it was 0.008 cm. when the pressure of the toluene was be-

Procedure

The experimental method required the constant presence of a body of pure liquid whose temperature may be arbitrarily adjusted so that the charcoal within the same sealed tube, but at higher temperature, may be exposed to any desired pressure of the vapor. It is vital that the charcoal should be drastically cleansed by heat and evacuation, and during this process the liquid to be used must remain within a sealed bulb (A in Fig. 1). Only after the final evacuation, when the main tube has been sealed, is this bulb A broken.

Preliminary Evacuation.—The charcoal and most of the sorption tube (see Fig. 1) were heated to 440° for seventy-five minutes during which a vacuum was very slowly applied. Evacuation was continued for three hours after the pressure had fallen below 10^{-4} mm. at 440°. (The bulb X with supporting hook rests on four projections in the glass to allow free passage.) Thereupon, after taking a zero reading of the length of the spring, the bottom of the tube containing the sealed bulb of liquid B, to which is attached by a solid stem a sealed bulb containing iron filings, is cooled with solid carbon dioxide or liquid air. The bulb is then raised by an electromagnet and broken. The whole is left at room temperature for some time to allow the vapor to displace foreign gases on the charcoal.

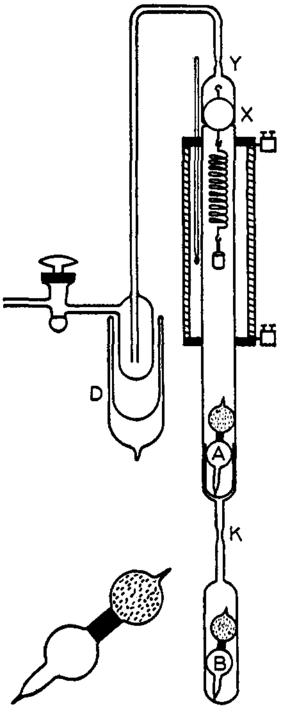

Fig. 1.—The sorption apparatus during evacuation, showing enlarged detail of the sealed bulb of liquid, B.

Final Evacuation.—The Dewar vessel D, filled with liquid air, is placed in position very gradually in order to avoid blowing charcoal out of the bucket. The tube is sealed off at K. The whole is then evacuated with the same care as before, but it takes several hours to bring the charcoal to 440° without blowing it out of the bucket. The time taken to attain a high vacuum is now much greater. While the vacuum pump is still working, the tube is finally sealed off at Y and is not reopened until the investigation is complete. The sealed bulb of liquid, A, is then cooled and broken as previously described.

Thermostats.—During an experiment the bottom of the sorption tube is immersed in mercury containing a thermometer. The whole sorption tube is placed within a wider glass tube which is heavily covered with asbestos on the outside and has a narrow slit in front and back running the length of the tube for purposes of observation. Outside this is wound heavy nichrome wire covered over again with asbestos. Current is led through the nichrome wire, using three terminals, a common one in the middle, and one at each end. Asbestos packing is placed outside the sorption tube at the middle terminal and at the top of the sorption tube, the furnace being closed above. A thermometer is placed between the sorption tube and the outside furnace beside the bucket of charcoal. In a blank experiment it was found that the thermometer placed within the vapor at 120° read 1.3° higher than that outside the tube. The whole is enclosed in a case with glass windows.

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tween 300 and 600 mm. This corresponds to 5×10^{-6} g. of toluene per sq. cm. of gold foil or a film approximately 5×10^{-6} cm. deep.

Commercial air ovens were found unsatisfactory, even although heating coils were inserted around the tubes where they passed through apertures. For low temperatures the apparatus was modified to admit of surrounding the bottom of the sorption tube with a Dewar flask containing a freezing mixture whose temperature was read by a pentane thermometer, a thermocouple being used to check constancy. All thermometers were calibrated against standards supplied by the National Physical Laboratory.

The charcoal was kept in contact with vapor for several days at 120° (or 205°) before any readings were taken, and not less than two hours was allowed between duplicate readings. Under these conditions Chapman observed but little effect of time. He avoided any condensation of liquid upon the charcoal.

TABLE I

ACETIC ACID.[a] "AIR C" CHARCOAL. 120° ISOTHERM BY P. F. C.

Experiment 5[b]

p	x/m	p	x/m	p	x/m[c]
23.1	0.204	88.9	0.334	169.8	0.383
27.3	.224	128.6	.359	142.6	.374
36.9	.255	132.0	.365	67.8	.321
37.9	.264	163.8	.379	39.5	.264
48.1	.280	175.3	.389	23.8	.221
58.6	.304	266.8	.414	16.4	.185
91.6	.329	483.4	.440	13.5	.162

[a] p_s = 794 mm. at 120°, 6500 mm. at 205°. [b] Final vacuum 10^{-5} mm. [c] Desorption.

TABLE II

ACETIC ACID. "AIR C" CHARCOAL. 120° ISOTHERMS BY H. P. L.

Experiment 1

p	x/m	p	x/m
14.5	0.178	330	0.424
77	.326	535	.435
125	.357	245	.414
127.5	.361	695	.450
204	.406	26.5	.24

Experiment 18

p	x/m	p	x/m
15	0.183	390	0.415
32	.258	193	.397
97.5	.361		

Experiment 19

p	x/m	p	x/m
14	0.198	660	0.461
30	.265	590	.457
58	.318	545	.453
505	.446	123	.381
276	.421	3.3	.082
725	.463		

TABLE III

ACETIC ACID. "STEAM D" CHARCOAL. ISOTHERMS BY H. P. L.

Experiment 2

At 120°		At 205°			
p	x/m	p	x/m	p	x/m
13.5	0.111	17.5	0.0269	1070	0.129
27.5	.112	41.5	.0435	202.3	.091
116	.141	125	.0770	2900	.140
202.3	.148	730	.122	4630	.141
153	.146	2195	.137	5450	.141
675	.156				
330	.150				
56	.133				

TABLE IV

TOLUENE.[a] "AIR C" CHARCOAL. 120° ISOTHERMS BY P. F. C.

Experiment 2[c]

p	x/m	p	x/m	p	x/m[b]
81.6	0.267	264.6	0.294	535.8	0.311
34.5	.238	383.4	.304	416.8	.304
51.1	.252	567.0	.310	225.2	.293
105.8	.276	613.2	.314	95.3	.270
131.9	.280	746.5	.318	26.3	.228
183.4	.290	869	.325	7.6	.199

Experiment 3[d]

p	x/m	p	x/m	p	x/m
68.3	0.296	641	0.354	68.3	0.300[b]
130.0	.321	752	.359	52.4	.290[b]
207.7	.332	325	.341[b]	28.4	.272[b]
355	.338	279.5	.340[b]	25.4	.263[b]
399.5	.342	144	.325[b]	7.8	.252[b]
528	.349	93.5	.311[b]	0.006[e]	.180[b]

[a] p_s = 988 mm. at 120°, 6451 mm. at 205°. [b] Desorption. [c] Preliminary evacuation five hours at 10^{-5} mm.; final evacuation six and one-half hours at 2×10^{-4} mm. Forty-five readings were taken, all of which fell on a smooth curve. The results are omitted from the graph because two turns of the spiral spring were caught in each other. [d] Preliminary evacuation seven hours at 10^{-5} mm.; final evacuation sixteen hours at 10^{-5} mm. [e] Liquid surrounded by solid carbon dioxide and ether.

TABLE V

TOLUENE. "AIR C" CHARCOAL. ISOTHERMS BY H. P. L.

Experiment 7		Experiment 10			
At 120°		At 120°		At 205°	
p	x/m	p	x/m	p	x/m
25	0.238	27	0.244	32	0.140
100	.289	62	.272	99	.190
178	.302	92	.283	2234	.291
223	.316	155	.298	263	.233
259	.323	230	.309	2583	.296
778	.332	460	.326	2965	.296
93.5	.293	790	.331	690	.272
74	.291	1020	.335	820	.276
67	.285	360	.321	850	.285
47.7	.281				

TABLE VI

TOLUENE. "AIR AND VACUUM B" CHARCOAL. 120° ISOTHERM BY H. P. L.

Experiment 9

p	x/m	p	x/m
845	0.140	820	0.142
27	.111	970	.141
107	.133	990	.144
200	.137	970	.141
250	.139	980	.141
720	.141	560	.141

TABLE VII

TOLUENE. "STEAM D" CHARCOAL. 120° ISOTHERM BY H. P. L.

Experiment 8

p	x/m	p	x/m
88	0.132	115	0.138
460	.139	92	.133
610	.139	80	.132
910	.142	25	.121

The data are given in Tables I–XIV where p is the vapor pressure in millimeters, and x/m is the sorption in grams per gram of charcoal. The vapor pressures were calculated using Dühring's rule with data obtained from Landolt-Börnstein "Tabellen," **1923**.[8] p_s, the saturation pressure, is the vapor pressure of the liquid at the temperature of the isotherm.

Table VIII

Toluene. "Steam E" Charcoal. 120° Isotherm by P. F. C.

Experiment 4[a]

p	x/m	p	x/m	p	x/m
32.0	0.180	493	0.212	223	0.204[b]
22.4	.174	571.3	.214	98.2	.196[b]
92.8	.195	658	.214	74.9	.193[b]
173.7	.202	854	.215	52.2	.188[b]
334.1	.208	474	.213[b]	7.8	.152[b]

[a] Preliminary evacuation eleven hours at 10^{-5} mm.; final evacuation sixteen and one-half hours at 10^{-4} to 10^{-5} mm. [b] Desorption.

Table IX

Hexane.[a] "Air C" Charcoal. 120° Isotherm by H. P. L.

Experiment 23

p	x/m	p	x/m	p	x/m
179	0.219	588	0.249	2100	0.268
279	.229	1050	.255	2800	.273
410	.239	1600	.263	1520	.263

[a] p_s = 2982 mm. at 120°.

Table X

Heptane.[a] "Air C" Charcoal. Isotherms by H. P. L.

Experiment 17

At 120°		At 120°	
p	x/m	p	x/m
42	0.226	490	0.269
285	.259	735	.274
618	.272	153	.251
848	.276	1260	.282
1080	.280		

Experiment 22

At 120°		At 120°	
p	x/m	p	x/m
51	0.219	270	0.262
108	.236	370	.264
119	.239	614	.266

Experiment 24

At 120°		At 205°	
p	x/m	p	x/m
46	0.219	59	0.150
90	.234	125	.166
138	.244	225	.185
452	.259	300	.194
578	.263	1530	.226
1047	.272	990	.219
1230	.284	1230	.228
1100	.279	1930	.231
660	.265	1700	.233
264	.252	690	.215

[a] p_s = 1367 mm. at 120°, 8000 mm. at 205°.

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[8] Data for toluene were obtained from N. W. Krase and J. B. Goodman, *Ind. Eng. Chem.*, **22**, 13 (1930).

Table XI

Octane.[a] "Air C" Charcoal. Isotherms by H. P. L.

Experiment 12

At 120°		At 120°		At 205°		At 205°	
p	x/m	p	x/m	p	x/m	p	x/m
20	0.249	515	0.289	340	0.235	1300	0.251
52	.263	550	.289	1540	.250	2075	.253
150	.280	630	.289	1650	.252	590	.238
380	.287	615	.289	1720	.252	44	.187

Experiment 13

At 120°		At 120°		At 205°	
p	x/m	p	x/m	p	x/m
37	0.259	320	0.286	38	0.185
47	.264	118	.281	115	.217
105	.279	87	.276	188	.227
180	.284	18	.243	650	.242
460	.288	60	.265	1290	.250
400	.288	200	.283	2150	.258

[a] p_s = 645 mm. at 120°, 4500 mm. at 205°.

Table XII

Decane.[a] "Air C" Charcoal. Isotherms by H. P. L.

Experiment 16

At 120°		At 120°		At 205°	
p	x/m	p	x/m	p	x/m
2.9	0.226	4	0.233	6	0.166
71	.273	59	.270	11	.184
14	.250	92	.274	165	.230
22	.263	158	.282	560	.247
115	.276	215	.291	1310	.256

Experiment 20

At 120°				At 205°			
p	x/m	p	x/m	p	x/m	p	x/m
26	0.267	44	0.281	265	0.246	314	0.254
42	.271	140	.295	2087	.264	110	.234
120	.292	177	.301	530	.256	15	.195
225	.303	215	.305	750	.261	10	.182
167	.306			875	.262		

[a] p_s = 245 mm. at 120°, 2314 mm. at 205°.

Table XIII

Acetone.[a] "Air C" Charcoal. 120° Isotherm by F. P. C.

Experiment 6

p	x/m	p	x/m	p	x/m
201.4	0.282	383	0.322	1353	0.373
209.5	.286	487	.335	1741	.388
253.5	.297	660	.349	1646	.391
307.7	.300	915	.389	2690	.404
437	.325	938	.366	3420	.411

[a] p_s = 5000 mm. at 120°.

TABLE XIV

METHYL ALCOHOL.[a] "AIR C" CHARCOAL. ISOTHERMS BY H. P. L.

At 40°		Experiment 25 At 40°		At 120°	
p	x/m	p	x/m	p	x/m
110	0.325	181	0.350	230	0.0459
31	.206	170[b]	.342	1200	.206
11	.082	165	.346	900	.174
90	.307	105	.326	2900	.289
31	.205	101	.324	3800	.309
46	.247	96	.320	2000	.257
113	.331	255	.355	1780	.249
200	.351	217	.350	720	.143

[a] p_s = 260.5 mm. at 40°, 4751 mm. at 120°. [b] The experiment was then left for one and one-half months before the further readings were taken.

Discussion

The most striking result of our experiments in this and the previous communications is that most of the sorption of vapors occurs at pressures amounting to only a few hundredths of the saturated vapor pressure at that temperature. Indeed, in several cases the sorption is only halved when the pressure is but one ten-thousandth of saturation. It needs no emphasis that this excludes the hypothesis of capillary condensation of liquid as a significant factor in the sorption of vapors by activated charcoal.

Differently activated samples of the same charcoal exhibit characteristically different behavior. In this as in previous communications, steam activated charcoal was not nearly as active as the best air activated charcoal. Oxidation of an appreciable fraction of the charcoal at 1140° yielded a highly active charcoal, capable

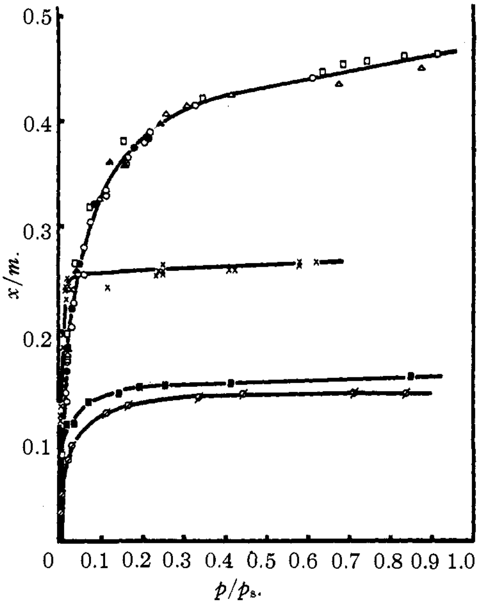

Fig. 2.—Sorption of acetic acid on charcoal.

○, P. F. C., Expt. 5, 120°, "Air C"; ●, P. F. C., Expt. 5, 120°, "Air C", desorption; △, H. P. L., Expt. 1, 120°, "Air C"; ▲, H. P. L., Expt. 18, 120°, "Air C"; □, H. P. L., Expt. 19, 120°, "Air C"; ■, H. P. L., Expt. 2, 120°, "Steam D"; ø, H. P. L., Expt. 2, 205° "Steam D"; ×, M. C. R.,[a] 120°, "Air and Vacuum B."

[a] Data obtained by Miss M. C. Rattue in 1925, using the method here described, the same conditions of time and temperature of evacuation and the same vacuum.

of sorbing from 30–45% of its own weight of various organic liquids. This charcoal, however, definitely does not show a "saturation value," for, with the possible exception of octane, the sorption continues to rise distinctly in the higher ranges of pressure.

Our results confirm the independent experiments of those who have previously studied the specimen of air activated charcoal that was given the long vacuum treatment at high temperature by Bakr. There is for practical purposes with a number of substances a saturation value. For example, reference to Table VI and Fig. 3 shows that when the pressure of the toluene vapor is only 23% of the vapor pressure of liquid toluene, the amount of sorption x/m is 0.139, while at 96% of the vapor pressure it is increased merely to 0.141. Indeed, the value of the sorption is, within the experimental error, 0.141 g. of toluene to 1 g. of charcoal throughout the upper half of the possible range of pressure. Other substances with the same charcoal may show far less tendency to approach a saturation value. This is notably the case with methyl alcohol and acetone.

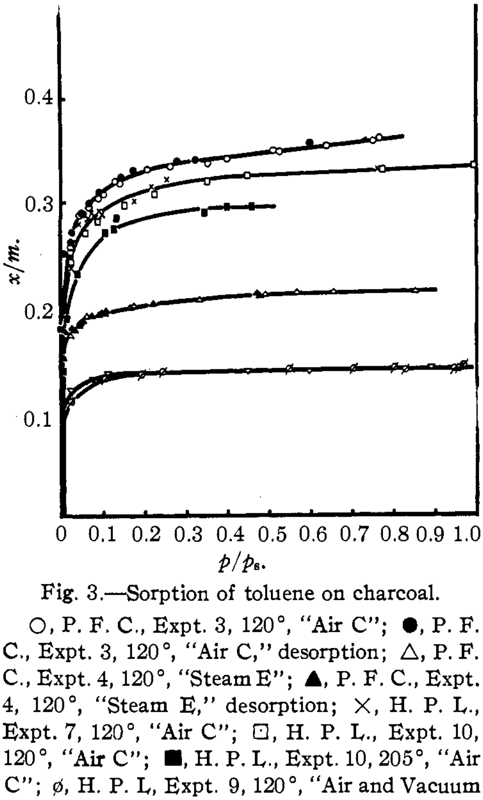

Fig. 3.—Sorption of toluene on charcoal.

○, P. F. C., Expt. 3, 120°, "Air C"; ●, P. F. C., Expt. 3, 120°, "Air C," desorption; △, P. F. C., Expt. 4, 120°, "Steam E"; ▲, P. F. C., Expt. 4, 120°, "Steam E," desorption; ×, H. P. L., Expt. 7, 120°, "Air C"; □, H. P. L., Expt. 10, 120°, "Air C"; ■, H. P. L., Expt. 10, 205°, "Air C"; ø, H. P. L, Expt. 9, 120°, "Air and Vacuum B"; ▽, H. P. L., Expt. 8, 120°, "Steam D."

We incline to regard the form and position of our sorption curves as being more typical of the true behavior of charcoal toward vapors than those obtained in the best studies from other laboratories, such as the results of Coolidge[9] and of Goldmann and Polanyi.[10] We base this, first, upon the consideration that in our experiments the residual impurities still present within the charcoal and the apparatus are constant throughout, and, second, upon our experience that very slight amounts of impurity, such as remain in spite of fairly good evacuation of the charcoal, suffice to lower the values of sorption observed, most notably in the lower range of pressures, so that the graphs assume more

[9] A. S. Coolidge, This Journal, **46**, 596 (1924).

[10] F. Goldmann and M. Polanyi, *Z. physik. Chem.*, **132**, 321 (1928).

nearly the appearance of those of the authors to whom specific reference has just been made. We have gained the impression that, with still more perfect evacuation, greatly prolonged, at the highest attainable temperatures, the typical sorption curve for charcoal would approach even more closely a form showing first a nearly vertical portion with the whole of sorption occurring at very low relative pressures, followed by an approximately horizontal line corresponding to no further increase of sorption over all the higher range of pressure.

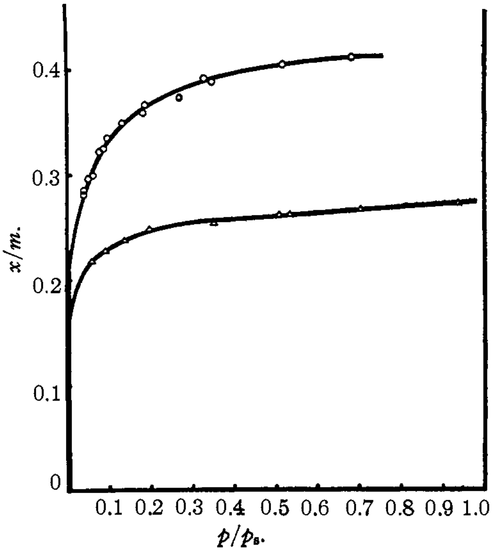

Fig. 4.—Sorption of hexane and of acetone by "Air C" charcoal at 120°. △, H. P. L., hexane, Expt. 23; ○, P. F. C., acetone, Expt. 6.

The form of this curve appears to be fairly independent of temperature. Throughout the higher range of sorption, the graphs for different temperatures run approximately parallel. Rise of temperature, as always, diminishes the weight of sorbed vapor which the charcoal can contain. The

Table XV

Measurements by H. P. L. with "Air C" Charcoal for $p/p_s = 0.5$

Vapor	120°	205°	Ratio
Hexane	0.262	..	..
Heptane	.270	(0.24)	1.125
Octane	.287	.254	1.130
Decane	.293	.262	1.118
Toluene	.327	.296	1.105
Acetic acid	.428	..	...
Acetone	.403	..	...
Methyl alcohol	.273	..	...

extent to which this occurs and the actual values for the sorption by Smith's "Air C" charcoal for $p/p_s = 0.5$ at 120 and 205° are compared in Table XV.

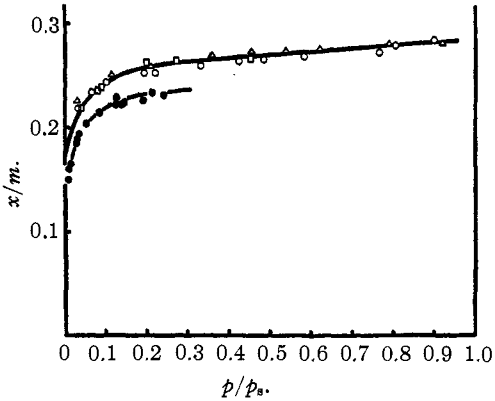

Fig. 5.—Sorption of heptane by "Air C" charcoal (H. P. L.). △, Expt. 17, 120°; □, Expt. 22, 120°; ○, Expt. 24, 120°; ●, Expt. 24, 205°.

The ratio for acetic acid was 1.21 for Bakr's "Air and Vacuum B" and 1.08 for Wright's "Steam D" charcoal. For methyl alcohol between 40 and 120° the ratio is 1.24.

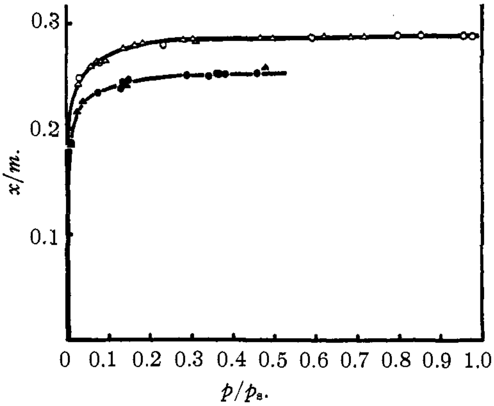

Fig. 6.—Sorption of octane by "Air C" charcoal (H. P. L.). ○, Expt. 12, 120°; ●, Expt. 12, 205°; △, Expt. 13, 120°; ▲, Expt. 13, 205°.

Bakr and McBain[11] observed that with Kahlbaum's (unactivated) sugar charcoal and their particular technique the weight of acetic acid which could be sorbed by 1 g. of charcoal was 1.34 times greater than the weight of toluene which could be sorbed under the same conditions. It is in-

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[11] A. M. Bakr and J. W. McBain, THIS JOURNAL, **46**, 2718 (1924).

teresting to note that in the experiments here recorded for activated sugar charcoals, "Air C," Wright's "Steam D" and "Air and Vacuum B," the corresponding ratios for acetic acid and toluene are 1.35, 1.35 and 1.36, respectively. Such comparisons can only be made when the vacuum technique for both cases is precisely similar. Likewise, in the present experiments (H. P. L.), the relative maximum amounts which can be sorbed by "Air and Vacuum B," Wright's "Steam D" and "Air C" charcoals are in the proportion of 1 to 1.04 and 2.38, respectively, for acetic acid and 1 to

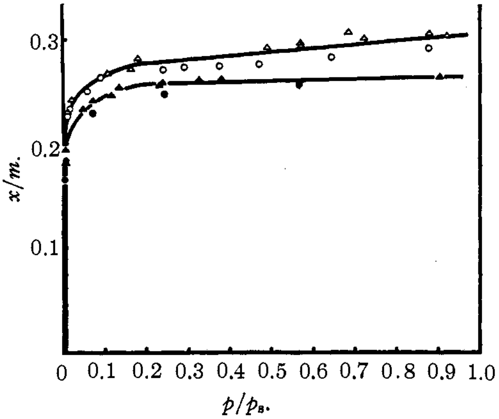

Fig. 7.—Sorption of decane by "Air C" charcoal (H. P. L.). ○, Expt. 16, 120°; ●, Expt. 16, 205°; △, Expt. 20, 120°; ▲, Expt. 20, 205°.

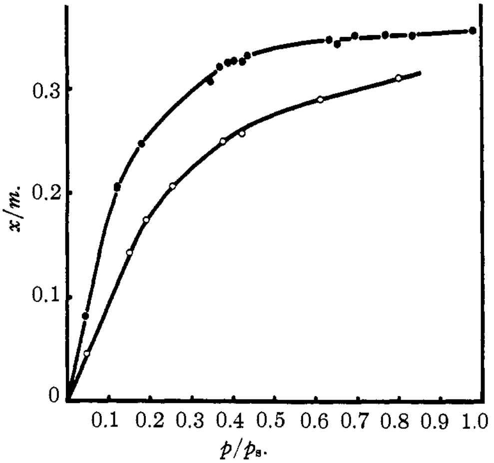

Fig. 8.—Sorption of methyl alcohol by "Air C" charcoal (H. P. L.). ○, Expt. 25, 120°; ●, Expt. 25, 40°.

1.03 and 2.37, respectively, for toluene. Activation thus exerts similar effects upon the sorption of both substances.

Our interpretation of sorption data with charcoal is that there is just room at each temperature within the charcoal for the close packed molecules to lie each in contact with carbon, fitting in as best they may in the open structure and incomplete composite lattices of the charcoal. We should not describe the temperature effect in terms of expansion of a liquid, compressed or otherwise, nor of a compressed atmosphere.

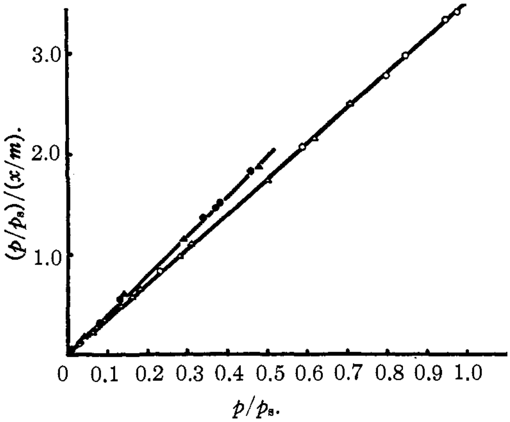

Fig. 9.—Langmuir graph, octane data of H. P. L. using "Air C" charcoal. ○, Expt. 12, 120°; ●, Expt, 12, 205°; △, Expt. 13, 120°; ▲, Expt. 13, 205°.

It is obvious that, if this conception be true, E. H. du Bois Reymond's term "adsorption" is as much of a misnomer as when applied to the molecules of water in a zeolite or the sodium or calcium atoms in a water softener such as permutite. Nor can sorption by charcoal be described as solid solution, because this presupposes complete homogeneity. We have in another communication called this type of sorption, "persorption."

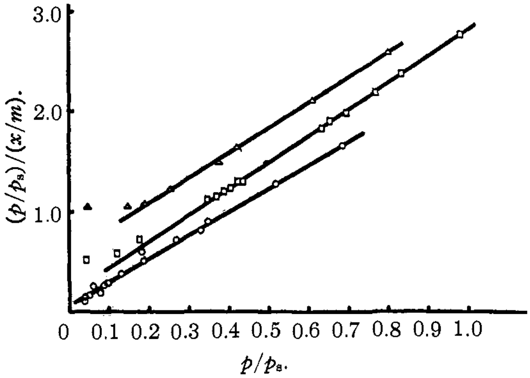

Fig. 10.—Langmuir graph for acetone and methyl alcohol, using "Air C" charcoal. ○, P. F. C., acetone, Expt. 6, 120°; △, H. P. L., methyl alcohol, Expt. 25, 120°; □, H. P. L., methyl alcohol, Expt. 25, 40°.

The ordinary empirical sorption formula, $x/m = kp^{1/n}$, fails to represent such data as these. Its logarithmic graph, instead of being a single straight line, becomes a flat curve concave downward, changing rather suddenly into a nearly horizontal line at the upper range of pressure. The most adequate formula for representing the ranges here investigated is that of Langmuir, $x/m = abp/(1 + ap)$, which should yield straight lines in graphs such as are shown in Figs. 9 and 10, which exhibit the same data as Figs. 4, 6 and 8, although these differ greatly from each other. Similar straight lines were obtained in our previous communications, including studies of sorption of nitrogen, nitrous oxide and ethylene up to sixty atmospheres. The only exception we have found is with methyl alcohol, for which there is a defect in sorption in part of the lower range of pressures. This may provisionally be attributed to the residual impurities which have been shown most greatly to affect this part of the isotherm. Acetone, like all the other substances, gives practically a straight line on the Langmuir diagram.

Inspection of the results with acetic acid shows that the results with different portions of a particular charcoal may be made reproducible. A close study of the data, as for example those for decane, shows that even with the mode of evaluation here employed, the time factor has not been wholly eliminated, although it is incomparably less than in experiments previously reported with less drastic procedures.

Conclusions

The thoroughness in evacuating and freeing activated charcoal from previously sorbed material, which is permitted by the use of the McBain–Bakr sorption balance in a sealed system, develops sorption isotherms of a new type in which nearly all the sorption occurs at very low pressures.

In some cases over the whole of the remaining range of higher pressures, there is practically no further sorption. The more drastic the preliminary purification of the carbon, the nearer is the approach to this type, which, therefore, appears to represent the true characteristic behavior of a pure vapor when sorbed by pure carbon. Data such as ours are adequately represented only by the Langmuir formula.

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