becomes $1/N^{\mathrm{a}} \int_0^{\varphi_{\mathrm{max.}}} \epsilon\, \delta\, \mathrm{d}\varphi$. This is clearly inadequate, as it omits the contribution from the internal energy change of the fluid in passing from the free to the adsorbed (compressed) state, which will (below the critical point) include the heat of vaporization.

Summary

The phenomenology and thermodynamic theory of adsorption systems are generalized and made applicable to the entire range of conditions within which the adsorbed substance normally exists as a fluid. Special attention is devoted to the corrections required when experiments are performed at high pressures. The conclusion is reached that several different methods of defining adsorption (all equivalent at low pressures) can advantageously be adopted, according to the purpose in hand. The consequences of adopting each of these definitions are followed in some detail, and illustrated, in the absence of suitable experimental material, by computations based upon the Polanyi theory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Adsorption at High Pressures. II

BY ALBERT SPRAGUE COOLIDGE AND HOLMES J. FORNWALT

Introduction

In order to provide experimental material illustrating the application of the ideas developed in the previous paper, we undertook to investigate the adsorption equilibrium between charcoal and several gases over a range of temperature and pressure extending both lower and higher than their critical regions. By working up to 100° and 100 atmospheres, we could accomplish this with carbon dioxide (critical point 31°, 73 atm.), nitrous oxide (c. p. 36.5°, 72 atm.) and silicon tetrafluoride (c. p. −1.5°, 50 atm.).

Materials and Apparatus

The charcoal used was a steam-activated coconut charcoal obtained from the National Carbon Company. The particles passed a 10- but not a 20-mesh sieve. In order to provide a basis for estimating the "skeleton" volume and the "pore" volume, we determined the apparent density by simple displacement (with boiling to expel gases) in several liquids, with the following results:

Liquid	Density	Specific volume
Mercury	0.629	1.590
Benzene	2.06	0.485
Ether	2.12	.472
(Graphite)	(2.25)	(.444)

We also determined an adsorption isotherm with benzene vapor at 20° as follows.

Pressure, mm.	13.5	20.5	39.5	50.0	70.5	74.0
Cc. ads. per g.	181.4	196.6	208.8	215.5	231.8	234.5

Upon extrapolating the isotherm to the saturation pressure of liquid benzene, we obtain 236 cc. of benzene vapor (measured at N. T. P.) as the maximum taken up by one gram of our charcoal.

The carbon dioxide was the last half of the contents of a commercial cylinder, and was used without special treatment to remove impurities, as the coincidence of adsorption and desorption points on a given isotherm seemed to prove that no significant amounts of foreign substances were present. The silicon tetrafluoride was prepared substantially by the method described by Booth and Germann,[1] in which the gas is generated by strongly heating barium fluosilicate, passed through a carbon dioxide cold trap and through glass wool and phosphorus pentoxide to remove water and hydrofluoric acid, and purified by distillation. Before use, each sample was condensed with liquid air and pumped. The density of the gas was carefully determined in a balloon, two runs giving 4.674 and 4.675 g. per liter at N. T. P. Nitrous oxide was taken from a cylinder. The density of the gas drawn from the top of the cylinder in the ordinary way was found too low; but when the cylinder was inverted the evaporated liquid possessed a normal density of 1.976, corresponding to 99.7% pure nitrous oxide, which was considered satisfactory.

The measurements were carried out with a quartz spring balance, from which the glass bucket containing the charcoal depended by a long platinum wire. The whole was housed in a nickel–silver tube, closed at the bottom, of sufficient length so that the upper part, enclosing the spring, did not change perceptibly in temperature during the necessary heating and cooling of the charcoal below. The movements of the spring were followed with a cathetometer through windows of plate glass, set with Wood's metal into a square steel block, which served as a union into which were screwed the lower and upper parts of the nickel–silver tube, as well as the connections to pump, gage and gas supply. Pressures up to 5 atmospheres were read on a mercury column. Above 5 atm. a dead-weight gage was at first used. Later, a large Bourdon gage was obtained, and by occasional comparison with the dead-weight gage was found satisfactory as to accuracy

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(1) Booth and Germann, *J. Phys. Chem.*, **21**, 81 (1917).

and sensitiveness, while far more convenient than the former. Indeed, the work with silicon tetrafluoride was greatly expedited by the use of the Bourdon gage, for the large amount of gas required to fill the dead-weight gage at a pressure of 100 atm., and the constant slow leakage with consequent change of pressure, would have greatly complicated the procedure. With the other gases, available in copious quantities at constant pressure in the tanks, the matter was less serious.

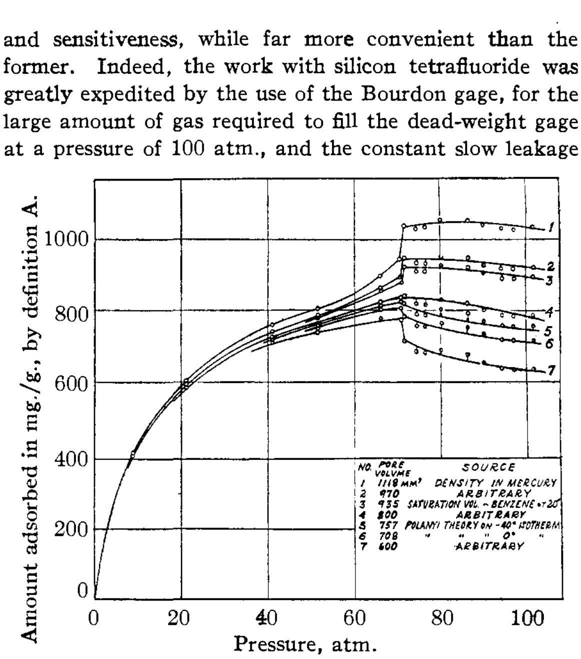

Fig. 1.—The effect of various pore volumes on the 30° adsorption isotherm of carbon dioxide as expressed by definition A.

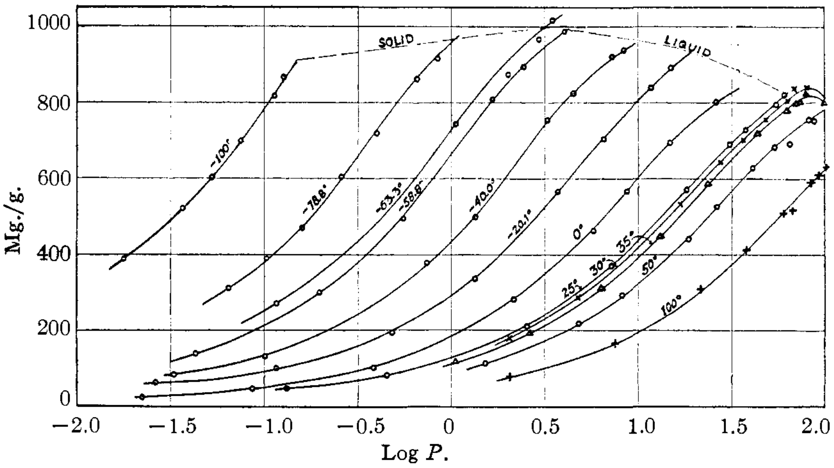

Fig. 2.—Carbon dioxide isotherms, definition A.

The first step in any determination was to outgas the charcoal for five or six hours at 550°, with the aid of a diffusion pump, which was kept operating during the subsequent cooling. The charcoal was then saturated with the substance under investigation (or charged to the maximum pressure, when working above the critical temperature), the temperature adjusted and held constant within 0.1°, and the system allowed to stand until constant pressure was observed. By successive removal of portions of substance, the isotherm was then traced downward as far as desired. A new isotherm was then determined without preliminary evacuation. In the case of silicon tetrafluoride, the procedure was modified, in that the −5 and 0° isotherms and the 25, 50 and 100° isotherms were determined simultaneously, each charge being brought in succession to each of the two or three temperatures mentioned before the withdrawal of a further portion.

Computation and Presentation of Results

At low pressures, the quantity of substance adsorbed, in mg. per g. of charcoal, was obtained simply by multiplying the observed spring extension by the appropriate constant. At higher pressures it was necessary to apply a correction for the buoyant action of the fluid on the moving system. To determine this, we ran series of blank experiments, in which all conditions were duplicated except that bucket and charcoal were replaced by a small weighted glass bulb. Particular care was exercised that if any great difference existed in the density of the fluid between bottom and top of the tube, the dividing meniscus or transition region should be formed along the length of the fine suspension wire. The correction was then the sum of two terms, the main term being the product of the volume of the bucket or bulb by the density of fluid in the lower part of the tube, while a small contribution came from the product of one-half the volume of the spring by the upper fluid density. Each blank experiment gave the sum of both terms; the small term could be estimated from approximate values of spring volume and fluid density, thus determining the main term, from which (with the known bulb volume) the lower fluid density could be fixed accurately. The values so found were in satisfactory agreement with the meager data in the literature. By working backward with the known volume of the bucket instead of the bulb, we could determine the proper correction for any adsorption experiment.

The result of this computation is the amount adsorbed according to definition C of the previous paper. To obtain the result by definition B (the accepted definition) it is necessary to apply a further buoyancy correction for the skeleton volume of the charcoal. This was taken as 0.472 cc. per g., as given by displacement with ether, the most penetrating liquid used, and in approximate agreement with the density of graphite. To produce definition A, a still further correction is needed to allow for the buoyancy of the fluid in the pore volume. From the experiments on saturation with benzene (assumed to have its normal liquid density) the pore volume is calculated to be 0.935 cc. per g. Applying the Polanyi treatment to the −40° isotherm measured with carbon dioxide, we obtain a maximum φ of 0.757 cc. (It should be noted that this result is entirely independent of any, even preliminary, assumption about either skeleton or pore volume, since all the resulting corrections are negligible at −40°.) If we assume that the volume of mercury displaced is the sum of pore and skeleton volumes, we get 1.118 cc. per g. This is certainly too large; evidently the mercury is prevented by surface tension from penetrating into a considerable volume of crevices which are nevertheless too large to count as part of the pore volume. Figure 1 shows an attempt to find a value of the pore volume which shall eliminate the discontinuity in the isotherm at saturation. The 30° isotherm for carbon dioxide is shown as calculated by definition A with various values of φ_2. (Direct rather than logarithmic pressures are here used.) The value 0.800 cc. per g. comes nearest to producing a continuous curve. (A break in slope is to be expected; see Fig. 1 of previous paper.) This value lies within the range suggested by other methods of approach, and was adopted in all the calculations.

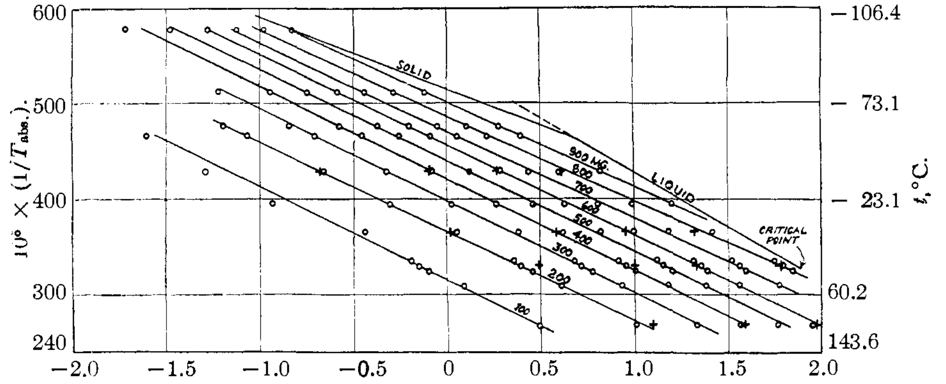

Fig. 3.—Carbon dioxide isosteres, definition A.

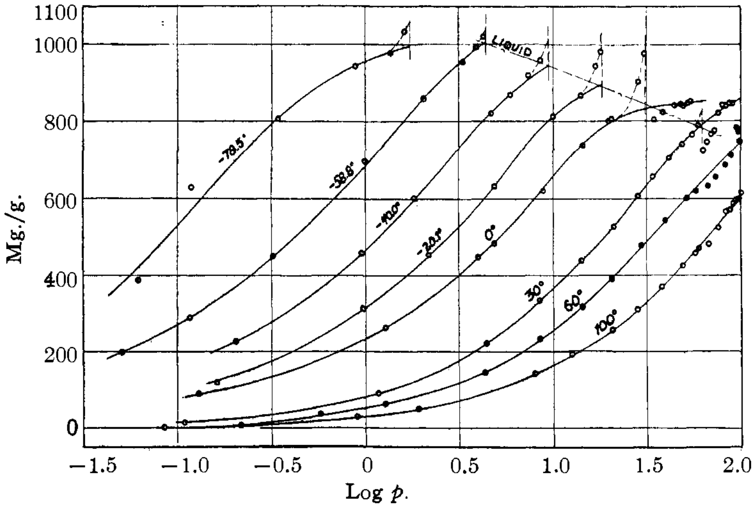

Fig. 4.—Nitrous oxide isotherms, definition A.

A couple of examples will elucidate the method of calculation:

Substance	CO_2	N_2O
Spring ext., mm.	4.45	−9.84
Equiv. wt., g.	0.808	−1.772
Press., atm.	7.21	54.4
Temp., upper layer, °C.	25	25

Density	0.0126	0.180
Half spring vol., cc.	.23	.23
Corr., g.	.003	.041
Temp., lower layer, °C.	25	0
Density	0.0126	.958
Bucket vol., cc.	1.32	1.160
Corr., g.	0.017	1.111
Amt. ads., g.	.828	−0.620
Charcoal, g.	2.330	1.685
N^c, g. per g.	0.355	−0.367
Skel. vol. corr.	.006	.452
N^b, g. per g.	.361	.085
Pore vol. corr.	.010	.767
N^a, g. per g.	.371	.852

The primary experimental data, N^c, and density of equilibrium fluid, δ, are reproduced in full in Tables I, II and III. In order to economize space, the derived quantities N^b and N^a are not tabulated, since they can readily be calculated, using for φ_1 and φ_2 either the values here suggested or others which the reader may prefer. Isotherms and isosteres for all points have been plotted, according to each definition. The resulting curves for definition A are shown in Figs. 2 to 7.

Table I

Carbon Dioxide Isotherms

P	δ	N^c
$T = -100°$		
0.018	0.000	388
.037	.000	522
.053	.000	603
.075	.000	699
.113	.000	817
.128	.000	866
$T = -77.8°$		
0.065	0.000	310
.103	.000	389
.158	.001	468
.258	.001	603
.401	.001	717
.655	.002	859
.845	.003	913
$T = -63.3°$		
0.116	0.000	272
1.066	.003	742
2.028	.005	870
2.963	.008	961
3.480	.009	1010
$T = -58.9°$		
0.043	0.000	139
.197	.001	300
.551	.002	494
1.671	.004	804
2.442	.006	887
4.005	.010	975
$T = -40.0°$		
0.033	0.000	84
.101	.000	132
.74	.002	377
1.35	0.003	496
3.27	.008	745
4.51	.011	810
7.27	.019	898
8.40	.022	910
$T = -20.1°$		
0.026	0.000	63
.116	.000	101
.483	.001	195
1.343	.004	333
3.713	.009	556
6.583	.016	685
11.76	.029	803
15.11	.039	842
$T = 0°$		
0.022	0.000	25
.087	.000	48
.384	.001	102
2.16	.004	278
5.76	.011	450
8.75	.018	545
14.90	.032	655
26.17	.062	723
$T = 25°$		
0.133	0.000	50
.45	.001	82
2.54	.004	206
7.21	.013	355
18.34	.035	527
31.00	.065	607
37.80	.085	621
54.88	.159	593
60.53	.201	565
$T = 30°$		
2.08	0.004	175
4.82	.009	277
16.95	.033	490
27.63	.057	569
36.73	.080	600
48.92	.120	601
63.28	.200	551
68.41	.262	503
$T = 30°$		
8.7	0.016	385
21.1	.042	542
41.0	.094	616
51.6	.131	605
66.2	.231	538
70.9	.320	438
71.6	.624	55
74.5	.668	− 24
76.5	.684	− 45
80.2	.706	− 59
86.4	.732	−102
90.1	.743	−135
94.4	.755	−165
97.0	.762	−177
101.5	.774	−188
$T = 33°$		
8.9	0.017	381
21.9	.043	538
39.9	.087	610
53.0	.132	603
68.5	.229	518
73.5	.302	457
78.0	.566	69
80.9	.634	12
84.9	.674	−35
92.8	0.719	−106
101.8	.750	−153
$T = 35°$		
0.534	0.001	87
1.042	.002	117
2.60	.005	187
6.33	.012	299
12.80	.024	418
23.67	.048	526
43.50	.099	593
62.37	.175	557
71.09	.238	496
73.82	.271	457
$T = 50°$		
1.535	0.003	112
4.807	.008	209
8.22	.013	278
18.76	.033	402
26.62	.048	467
41.61	.083	523
53.70	.117	534
64.95	.155	496
82.6	.241	451
88.3	.282	395
102.7	.437	58
$T = 100°$		
2.06	0.003	75
7.59	.012	153
21.46	.034	265
37.70	.060	336
60.61	.100	383
85.2	.154	396
92.7	.172	392
100.0	.191	393
103.0	.198	376

Table II

Nitrous Oxide Isotherms

P	δ	N^c
$T = -78.5°$		
0.06	0.000	388
.12	.000	629
.35	.001	806
.90	.003	940
1.36	.004	974
1.60	.007	1028
$T = -58.5°$		
0.05	0.000	200
.12	.000	290
.33	.001	450
1.00	.003	694
2.06	.005	853
3.32	.009	944
3.91	.010	982
4.28	.011	1009
$T = -40.0°$		
0.20	0.001	227
.96	.003	453
1.84	0.005	594
4.66	.012	807
5.97	.015	851
7.46	.019	894
8.62	.022	932
$T = -20.1°$		
0.16	0.001	119
.98	.003	308
2.17	.006	446
4.90	.013	615
10.0	.026	780
14.2	.036	821
16.9	.044	888
18.2	.047	920
$T = 0°$		
0.13	0.000	89
1.29	.003	260
3.98	.009	437
4.90	.011	470

TABLE II (*Concluded*)

P	δ	N^c
8.9	0.021	594
14.5	.035	691
19.8	.050	738
20.5	.051	743
28.4	.075	809
30.7	.084	872
34.7	.920	−365
39.2	.930	−359
44.9	.942	−355
48.6	.949	−362
49.8	.951	−367
53.1	.956	−367
54.4	.958	−367
T = 30°		
0.11	0.000	15
1.17	.002	88
4.46	.008	213
8.48	.017	314
14.3	.030	400
21.1	.046	468
28.8	.067	523
34.2	.083	552
41.5	.107	569
49.1	.138	565
55.7	.174	545
60.0	.208	526
64.1	.696	−161
66.8	.722	−171
70.3	.748	−184
72.9	.764	−196
76.9	.787	−179
81.1	.805	−182
84.5	.816	−197
88.1	.826	−202
91.7	.834	−213
T = 60.3°		
0.22	0.000	8
0.57	0.001	34
1.28	.001	62
4.36	.004	141
8.55	.008	225
14.27	.021	292
20.38	.033	351
29.70	.054	409
39.42	.080	444
52.0	.115	454
58.5	.134	452
67.4	.160	429
75.5	.188	417
83.5	.227	398
90.3	.285	352
95.3	.374	308
98.3	.412	250
100.5	.429	203
T = 100°		
0.08	0.000	1
.90	.000	28
1.93	.001	50
4.34	.003	90
8.00	.006	136
12.56	.011	180
20.86	.022	231
28.3	.033	272
38.4	.051	306
49.6	.073	333
57.9	.090	345
60.0	.094	349
67.8	.107	345
76.1	.122	370
84.7	.138	392
89.0	.150	380
92.2	.161	381
95.7	.173	377
99.6	.189	358
102.8	.202	359

TABLE III

SILICON TETRAFLUORIDE ISOTHERMS

P	δ	N^c
T = −100°		
0.072	0.000	809
.134	.001	970
.246	.001	1105
.355	.002	1160
.453	.003	1189
.555	.004	1212
.645	.004	1240
1.154	.007	1274
T = −78.5°		
0.11	0.001	670
.24	.002	792
.43	.003	928
.97	.006	1088
1.41	.009	1148
1.96	.012	1180
2.43	.015	1211
2.80	0.017	1248
2.88	.018	1250
T = −58.8°		
0.16	0.001	638
1.01	.006	916
2.01	.011	1046
2.69	.015	1091
3.83	.022	1136
7.34	.047	1247
T = −40.0°		
0.14	0.001	527
1.00	.005	785
1.94	.011	888
3.27	.018	964
5.68	.032	1039
8.94	.053	1068
10.74	.066	1066
T = −20.1°		
0.11	0.000	410
1.17	.004	676
3.17	.014	828
6.17	.031	917
17.0	.107	980
21.7	.153	964
21.9	.155	952
23.8	.178	947
25.4	.199	927
28.5	.248	862
T = −10°		
0.49	0.002	511
1.00	.005	605
2.02	.009	708
4.45	.021	814
9.30	.047	903
16.8	.094	933
23.3	.152	914
29.6	.230	810
32.8	.280	798
35.9	.342	694
T = −5°		
0.66	0.003	490
.99	.004	542
3.82	.016	742
8.43	.039	840
17.3	.094	885
26.0	.168	870
34.0	.271	771
38.0	.346	704
45.6	.580	392
48.2	.772	295
52.4	.850	59
57.2	.927	− 42
61.9	.979	− 79
65.6	1.011	−117
69.0	1.034	−147
T = 0°		
0.67	0.003	470
1.00	.005	519
3.83	.020	712
8.70	.040	811
16.7	.085	858
26.0	.153	835
34.0	.236	763
39.7	.317	682
43.6	.392	589
50.7	.587	352
55.1	.723	171
59.2	0.815	67
63.7	.883	23
70.2	.954	−85
72.4	.972	−107
T = 25°		
0.46	0.002	273
2.88	.012	495
9.83	.043	647
18.91	.088	708
27.40	.136	707
37.0	.201	673
43.8	.257	631
51.3	.327	548
51.7	.331	565
57.8	.395	517
68.0	.512	384
73.0	.570	310
77.7	.615	224
89.0	.743	110
T = 50°		
0.49	0.002	227
2.96	.011	404
9.97	.039	547
19.10	.080	612
28.4	.125	630
38.1	.179	616
46.3	.232	588
53.5	.280	576
54.1	.284	562
62.5	.343	518
72.2	.416	450
79.1	.466	386
85.9	.514	334
93.7	.566	271
T = 100°		
0.54	0.002	179
3.15	.010	282
10.9	.035	402
20.2	.068	476
30.7	.108	493
40.9	.151	499
52.6	.207	489
57.7	.233	486
58.5	.237	494
67.9	.283	469
81.1	.346	423
88.6	.381	397
95.7	.412	368
100.0	.430	351

The corresponding curves for the other definitions are not reproduced here, as their complicated shape renders them less suitable for indicating the degree of consistency among the individual results. They are very similar to Figs. 2 and 3 of the preceding paper; the characteristic overlapping of the isotherms near the critical point is beautifully displayed.

Test of Polanyi Theory

TABLE IV

FUNDAMENTAL ϵ–φ CURVE

ϵ	φ	ϵ	φ
5000	0	1000	362
4000	12	750	470
3000	45	500	597
2500	74	250	686
2000	127	100	723
1500	212	0	743

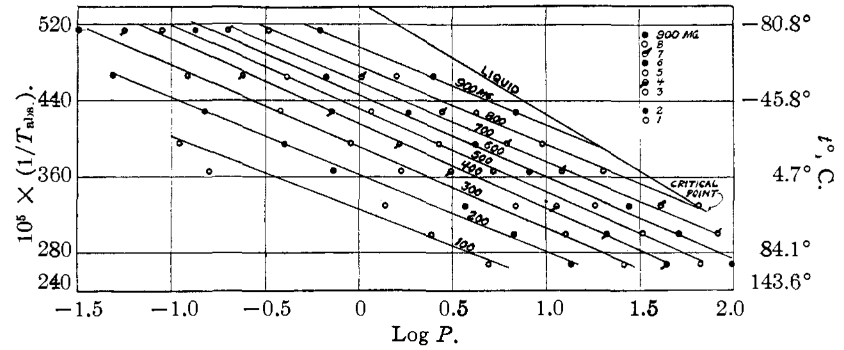

Fig. 5.—Nitrous oxide isosteres, definition A.

We could test the Polanyi theory only in the case of carbon dioxide, for which good equations of state are known. We used the method of Lowry and Olmstead,[2] retaining, however, all terms in their eq. (15) because of the high outside gas density. We followed them in using observed vapor pressures and coexisting densities, applying the necessary correction to ϵ in going from gas to liquid. For this reason the results are not quite comparable to those of the calculations in the preceding paper. The fundamental ϵ–φ curve is given in Table IV. The calculated isotherms are shown in Fig. 8 as black circles, the solid lines being the experimental isotherms, according to each of the three definitions. An additional comparison with experiment is shown in Fig. 6, in which the crosses show the Polanyi isosteres (points interpolated at equal round values of N^a from the several calculated isotherms).

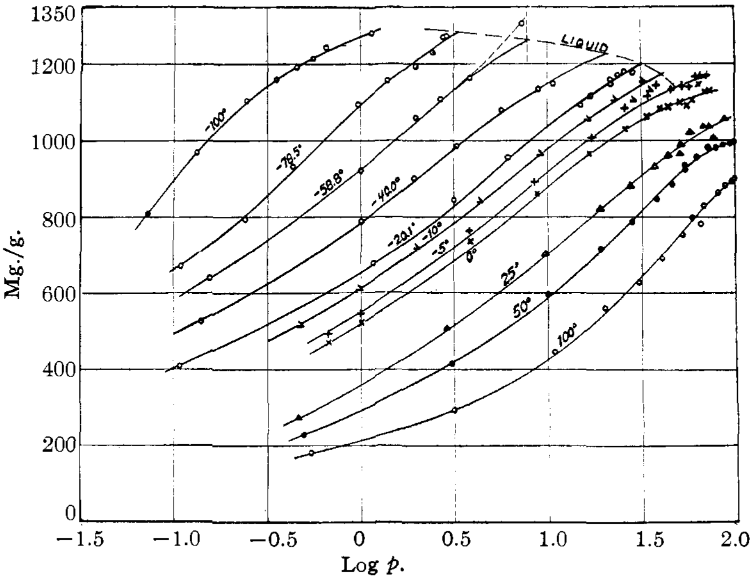

Fig. 6.—Silicon tetrafluoride isotherms, definition A.

Discussion

The general picture of adsorption phenomena at high pressures, in the case of carbon dioxide, is evidently in quite good agreement with the predictions of the Polanyi theory. This is all the more striking in view of the magnitude and uncertainty of the corrections involved in reducing the experimental data to a form suitable for comparison, and the fact that these corrections were determined by independent means. Nevertheless, a number of small systematic discrepancies appear to exist. (The large discrepancy at −78.8° is doubtless due to an unwarranted extrapolation of the equation of state.) The amount adsorbed at 0° is a little smaller than the theory predicts. As this discrepancy also shows up on the isosteres (Fig. 3), and is not found in the work of other authors, it is probably assignable to experimental error. A discrepancy in the opposite direction appears in the lower portions of the 30 and 100° isotherms. Here Fig. 3 shows that it is the observed, rather than the calculated, points which fall upon straight isosteres,

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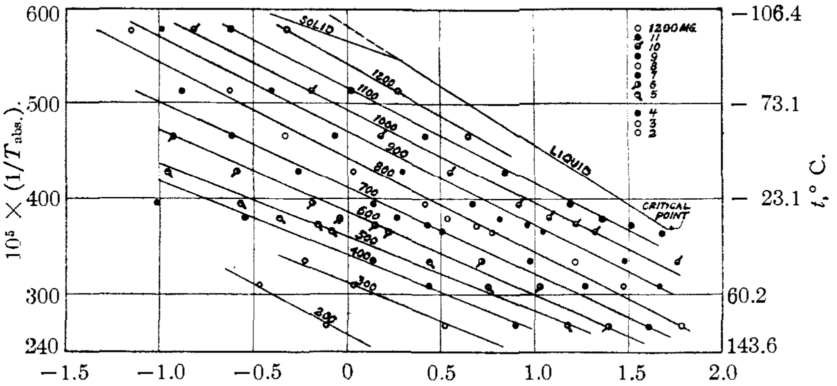
[2] H. H. Lowry and P. S. Olmstead, *J. Phys. Chem.*, **31**, 1601 (1927).

which seems good evidence in their favor. Finally, there is some divergence between the assumed pore volume, 0.800 cc. and the maximum adsorption space of the ϵ–φ curve, 0.744 cc.

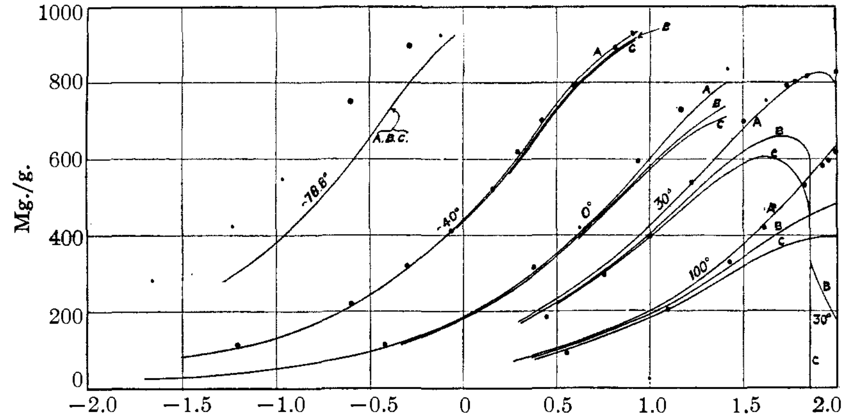
The isosteres of carbon dioxide continue practically straight to temperatures well below the freezing point, indicating that in the specific heat of the adsorbed layer there is nothing in the nature of heat of fusion. This has been found true also of water[3] and benzene.[4] Carbon dioxide resembles water, and differs from benzene, in that the heat of adsorption is less than the heat of sublimation.

A matter of much interest is the manner in which the isotherms approach saturation. It has been shown[4] by one of us that in the case of benzene vapor, if saturation is caused by reaching the vapor pressure of the solid, the isotherm terminates abruptly; but if the vapor pressure of the liquid is being approached, there is a small transition section in which the isotherm curves upward and becomes asymptotic to a vertical line so that no saturation capacity can be strictly defined. It is customary (as in Polanyi calculations) to ignore this transition section, which seems to belong to a different phenomenon from the main one being studied, possibly being due to deposition of deep layers upon the outside surface of the pieces of adsorbent. The present experiments are not on a fine enough scale to show this phenomenon reliably, but the transition section is clearly indicated in the nitrous oxide isotherms (Fig. 4). The irregularities in the curves near the critical point (especially in Fig. 1, which magnifies this region) may be due in part to this effect; another cause may be the difficulty of controlling the buoyancy correction where the fluid density fluctuates so rapidly. Figure 1 shows a tendency for N^a to decrease slightly with further rise in



Log p.

Fig. 7.—Silicon tetrafluoride isosteres, definition A.



Log p.

Fig. 8.—Comparison of Polanyi values with experimental definition A isotherms: ●, calculated Polanyi values. The solid lines are experimental curves plotted by definitions A, B, C.

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[3] A. S. Coolidge, THIS JOURNAL, **49**, 708 (1927).

[4] A. S. Coolidge, *ibid.*, **46**, 596 (1924).

pressure, in contradiction to all expectations. This effect is probably spurious; the other substances do not show it.

While the isotherms of all three fluids are closely similar, the isosteres of silicon tetrafluoride deviate systematically from nearly straight lines, and almost seem to belong to portions of different sets, as though some permanent change had affected the adsorbent between the work at lower and at higher temperatures. Unfortunately this was not noticed until the apparatus had been demolished and control experiments made impossible.

Summary

Adsorption equilibrium between charcoal and three gases is investigated with particular attention to the region near the critical point. The results are of the general nature anticipated. In the case of carbon dioxide, a successful application of the Polanyi theory has been made.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Hydrazoic Acid[1]

BY EDWARD C. FRANKLIN

Some of the methods for the preparation of hydrazoic acid and a majority of its reactions lead fairly definitely to the conclusion that it is an ammono nitric acid. Other methods of preparation and a few of its reactions are best explained on the assumption that it is a cyclic nitrous acid acid hydrazide, while certain minor considerations lend support to the view that it is a cyclic ammono hyponitrous acid.

The tautomeric properties of hydrazoic acid are discussed in another place.[2] Here an account is given of experimental work which supports the view, first expressed by Turrentine,[3] that hydrazoic acid may be regarded an ammono nitric acid.

Ammonolysis of Potassium Aquonitrate to Potassium Ammononitrate.—On the assumption that hydrazoic acid is an ammono nitric acid it was surmised that it might be possible to obtain the acid by the ammonolysis of aquo nitric acid say in accordance with the one or the other of the equations, $HONO_2 + 2NH_3 = HN{=}N{\equiv}N + 3H_2O$ or $KONO_2 + 2NH_3 = KN{=}N{\equiv}N + 3H_2O$. As a matter of fact no such reactions take place when either ammonium nitrate or potassium nitrate is heated in liquid ammonia solution. However, it was found that hydrazoic acid in the form of its potassium salt, together with potassium hydroxide, is formed when a liquid ammonia solution containing potassium aquonitrate and potassium amide is heated for a time at temperatures around 80–90°. It was later found that higher temperatures up to 130 to 140° give better yields in a shorter time. At still higher temperatures, 200° or higher, liberal quantities of nitrogen are set free and the yield of potassium azide is lower. Representing the reaction involved by the equation $KONO_2 + 3KNH_2 = KN{=}N{\equiv}N + 3KOH + NH_3$, and assuming that the nitric acid nitrogen present in potassium aquonitrate persists as such in potassium azide, it will be clear that potassium aquonitrate undergoes ammonolysis to form a potassium ammononitrate.

A liquid ammonia solution containing potassium nitrate and potassium amide was heated in a sealed glass tube at a temperature of 90° for three hours. After cooling, a crystalline precipitate, which was later identified as potassium hydroxide, was observed to have settled to the bottom of the tube. After opening the tip of the tube and allowing the liquid ammonia to evaporate away, the solid residue left behind was dissolved in water and the solution thus obtained was rendered slightly acid by means of dilute nitric acid. Addition of ferric chloride to a portion of this solution gave the brown coloration described by Curtius as a test for hydrazoic acid. On adding silver nitrate to the remainder of the solution, a white precipitate was formed which was filtered off, washed, and after dividing into small portions, dried in an exsiccator over sulfuric acid. The dried solid, when touched with a hot glass rod or when struck with a hammer, exploded with the powerful detonation characteristic of silver azide.

Following the above described procedure and using potassium amide in excess, Harker obtained yields of potassium azide as high as 75% of the amount calculated on the basis of the above equation. By using sodium nitrate and sodium amide

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[1] The laboratory work upon which this report is based was done by the author, Faw Yap Chuck, Thesis, Stanford University, 1925, J. B. Harker, Thesis, Stanford University, 1927, and E. S. Goodyear, Thesis, Stanford University, 1928.

[2] "The Nitrogen System of Compounds," American Chemical Society Monograph, 1934.

[3] Turrentine, THIS JOURNAL, **34**, 385 (1912).