thoroughly with ethanol, then water. After drying, the product weighed 16.5 grams and melted at about 265° C. Two recrystallizations from acetonitrile raised the melting point to 274–4.5° C. Anal. Calcd. for $C_{20}H_{12}N_2S_2$: C, 69.7; H, 3.5; N, 8.1; S, 18.6. Found: C, 69.7; H, 3.4; N, 8.0; S, 18.5.

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Adsorption of Methane on Carbon at Temperatures to 121° C. and Pressures to 650 Atm.

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Gas adsorption isotherms and isobars are presented for the methane–Spheron-6 system for six isotherms ranging from 37.8° to 121.1° C. Data were obtained utilizing a high pressure, constant temperature, volumetric apparatus at pressures up to 650 atm.

CONDITIONS surrounding the production of large amounts of natural gas and the difficulties involved in separating the hydrocarbon components require continuing research in the area of gas adsorption at high temperatures and pressures. Gilmer and Kobayashi (*4*) have published data on adsorption of methane on silica at pressures up to 135 atm., while Frolich and White (*3*) report methane adsorption on carbon up to 140 atm. Both investigators report a Type I isotherm which agrees with other reports (*1, 2, 5, 6*) on carbon-methane adsorption.

This communication will report fundamental gas adsorption data at temperatures and pressures above the critical point of gas in the gas-solid system.

EXPERIMENTAL

Materials. Carbon black (Cabot Corp.), bearing the designation Spheron-6, served as the adsorbent for all isotherms. Density of the adsorbent was 1.8 grams per cc. Surface area of the solid was 123 sq. meters per gram, determined by the classical BET low temperature adsorption of nitrogen where monomolecular adsorption was assumed. The adsorbate was research grade methane having a stated purity of at least 99.65%. Helium was used to determine dead space volume.

Equipment and Methods. The apparatus (Figure 1) was constructed of stainless steel. The volumetric system was composed of four thick-walled, constant volume cells. The adsorbent was enclosed in the high pressure cell, where

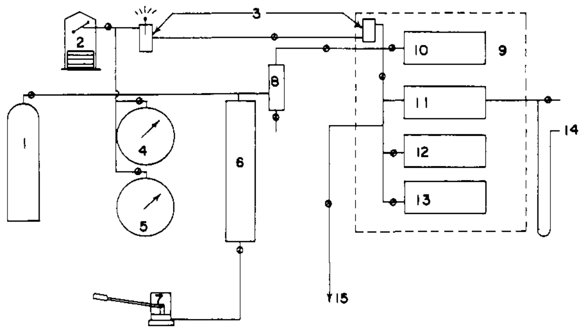

Figure 1. Flow diagram of hydraulic system

1. Gas cylinder
2. Dead weight gage
3. Mercury level cell
4. 15,000 P.s.i. gage
5. 3000 P.s.i. gage
6. Pressure transmitter
7. Pressure pump
8. Trap
9. Air bath
10. H. p. cell
11. L. p. cell No. 1
12. L. p. cell No. 2
13. L. p. cell No. 3
14. Manometer
15. To vacuum system

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methane gas was compressed at constant temperature until the maximum desired pressure was obtained.

Temperature was controlled by thermostated air bath with forced air circulation. Calibrated copper-constantan thermocouples were used in conjunction with a Leeds & Northrup K-3 potentiometer to determine temperature.

The desorption cycle was taken after temperature equilibrium was obtained. The low pressure cells were evacuated, using a two-stage mercury diffusion pump and a mechanical pump. Immediately prior to expanding gas into the low pressure cells, the pressure in the low pressure system was read from a Stokes McLeod gage. Gas was then allowed to expand from the high pressure system until a pressure of approximately 1 atm. in the low pressure system was reached. After noting pressure and temperature readings in both systems, the low pressure system was evacuated and the process repeated. Stepwise gas withdrawals from the adsorption cell were continued until expansion into the low pressure system caused no appreciable change in manometer reading. A complete description of the equipment and experimental procedure can be found elsewhere (*7*).

The adsorbed quantity was calculated by subtracting the total amount of gas withdrawn from the quantity in the adsorption cell at the adsorption pressure. Mathematically, the adsorbed quantity may be expressed as

$$N_k = -\frac{P_k \bar{V}}{Z_k R T} + \frac{V}{RT} \sum_{i=k}^{n} \left(\frac{P_i}{Z_i} \right) \tag{1}$$

where $1 < k < n$.

Masukawa (*8*) has shown that this expression describes Gibbs' adsorption according to the thermodynamic definition. In this case, dead space volume $\bar{V}$ includes the volume of free gas space in the adsorption cell as well as the volume of the adsorbed layers.

Data reported here were gathered using a single adsorbent bed weighing 14.6 grams enclosed in a steel adsorption cell. Total dead space volume, $\bar{V}$, of the cell and connected tubing was 66.4 cc. This value was determined by expansion of helium into the adsorption cell with the assumption that helium was not adsorbed. The sample was thoroughly outgassed between runs.

Compressibility factors used in this investigation were those reported by Sage and Lacey (*9*). However, as a part of experimental procedure, compressibility factors for methane were determined during this investigation.

Gas compressibility factors were determined by taking an adsorption isotherm with no adsorbent in the sample chamber. The amount of gas in the sample chamber was calculated at each pressure increment by using the ideal gas law. The ratio of the calculated quantity of gas in the cell to the measured quantity was taken as the compressibility factor. Data taken in this manner agreed to within ±0.3% with smoothed values reported by Sage and Lacey.

PRECISION

Several measurements of dead space volume agreed within 1%. Volume was the most critical parameter determined. Maximum error arising from erroneous volume measurement could amount to 10% of the gas adsorbed. Temperature was measured to within ±0.05° C. during any isotherm. This variation could result in a maximum absolute error of 0.2% of the gas adsorbed. This error would occur at maximum pressure on the low temperature isotherm. Pressure measurements were taken with an accuracy of 0.05% for high pressure measurements. Low pressure readings were taken with a cathetometer reported to be precise at 0.02 mm. These pressure measurements were sufficient to limit errors to within 1% of the amount adsorbed.

RESULTS

Figures 2 and 3 present isotherms and isobars for the solid-gas system. The isotherms take the classical Type I shape indicating increasing adsorption with steadily increasing pressure. The curves also show decreasing adsorption with increasing temperature. Table I lists raw data for the methane-carbon isotherms.

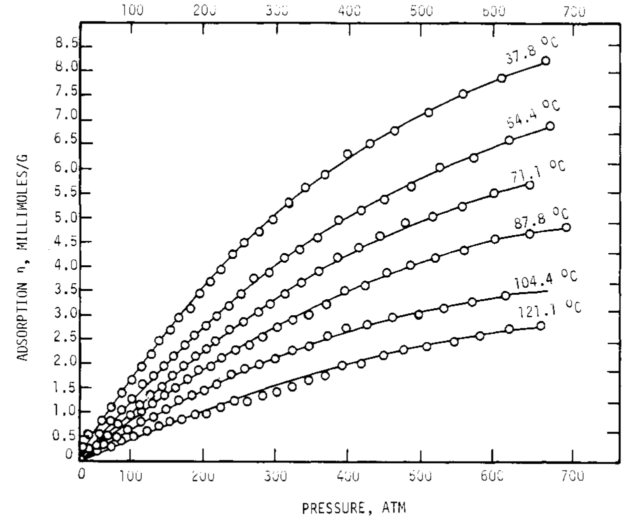

Figure 2. Adsorption isotherms of methane on Spheron-6

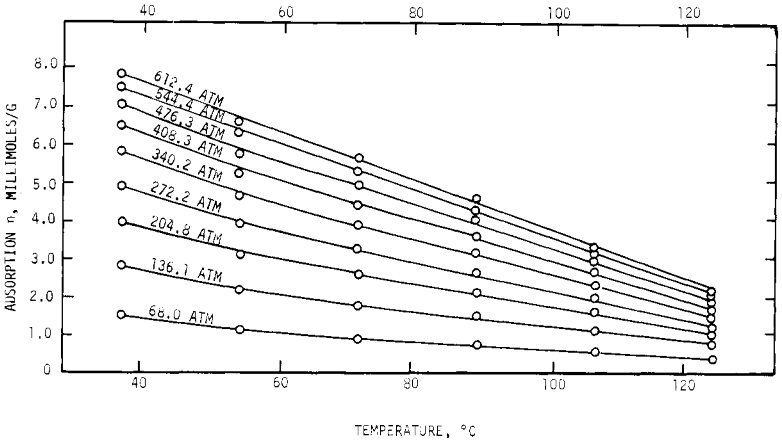

Figure 3. Adsorption isobars of methane on Spheron-6

Table I. Adsorption of Methane on Spheron-6

Adsorption Pressure, Atm.	Adsorbed Quantity, Mmoles/ Gram	Adsorbed Volume, Cc./G. Mole	Adsorption Pressure, Atm.	Adsorbed Quantity, Mmoles/ Gram	Adsorbed Volume, Cc./G. Mole	Adsorption Pressure, Atm.	Adsorbed Quantity, Mmoles/ Gram	Adsorbed Volume, Cc./G. Mole
	37.8° C.			71.1° C.			104.5° C.	
647.97	8.24	23.00	627.69	5.71	21.60	640.62	3.63	22.47
586.94	7.88	19.22	576.66	5.55	18.70	592.31	3.44	19.51
532.98	7.53	16.73	531.75	5.27	16.68	546.72	3.30	17.31
485.89	7.18	14.99	490.24	5.08	15.13	506.23	3.18	15.70
442.88	6.96	13.65	452.13	4.95	13.92	468.13	3.04	14.41
405.32	6.52	12.63	418.79	4.66	12.98	433.77	2.98	13.39
372.39	6.35	11.83	388.17	4.44	12.20	401.79	2.82	12.54
342.32	5.90	11.16	359.73	4.21	11.54	372.53	2.74	11.83
315.43	5.64	10.61	333.19	3.91	10.97	344.28	2.57	11.20
291.41	5.33	10.15	309.23	3.69	10.49	319.45	2.37	10.69
269.57	4.95	9.75	287.26	3.48	10.07	294.95	2.30	10.21
249.30	4.76	9.39	266.37	3.25	9.69	272.50	2.11	9.80
230.79	4.47	9.08	246.64	3.09	9.34	251.06	2.00	9.42
213.43	4.26	8.79	228.26	2.87	9.04	230.31	1.89	9.07
197.37	3.94	8.53	210.23	2.73	8.74	210.57	1.78	8.75
182.20	3.67	8.30	193.36	2.51	8.47	192.00	1.59	8.45
167.57	3.43	8.07	177.03	2.33	8.22	173.69	1.45	8.16
153.62	3.15	7.86	161.10	2.16	7.97	155.66	1.35	7.89
139.95	2.91	7.65	145.59	1.97	7.73	137.90	1.24	7.62
126.41	2.69	7.44	130.48	1.75	7.50	120.75	1.08	7.36
113.07	2.44	7.24	115.51	1.54	7.28	103.54	0.94	7.09
99.66	2.20	7.04	100.40	1.36	7.05	86.39	0.80	6.83
86.32	1.91	6.83	85.36	1.16	6.81	69.24	0.65	6.55
72.58	1.66	6.61	70.26	0.95	6.57	51.89	0.51	6.25
58.63	1.38	6.37	54.88	0.75	6.31	34.47	0.35	5.92
44.27	1.10	6.11	39.23	0.54	6.02	23.45	0.25	5.67
29.23	0.85	5.81	23.24	0.32	5.67	12.15	0.17	5.35
13.85	0.55	5.41	7.11	0.05	5.15	1.10	0.01	4.72
4.53	0.29	5.02						
0.51	0.03	4.59		87.8° C.			121.1° C.	
	54.5° C.		676.68	4.86	25.29	642.12	2.82	22.58
			625.31	4.71	21.45	598.30	2.71	19.84
654.10	6.93	23.45	577.34	4.62	18.73	557.61	2.60	17.79
597.08	6.62	19.77	535.49	4.35	16.83	520.79	2.47	16.25
547.26	6.24	17.33	496.37	4.20	15.35	484.79	2.38	14.95
501.13	6.08	15.51	460.30	4.05	14.16	452.13	2.33	13.92
461.66	5.69	14.20	427.50	3.92	13.21	421.72	2.20	13.06
424.71	5.41	13.14	398.24	3.63	12.45	393.75	2.08	12.34
390.89	5.19	12.27	370.00	3.54	11.77	367.28	1.98	11.71
360.07	5.01	11.55	343.80	3.25	11.19	342.58	1.75	11.17
332.71	4.63	10.96	319.44	3.09	10.69	318.90	1.67	10.68
308.01	4.37	10.46	296.99	2.90	10.25	296.92	1.52	10.25
284.75	4.22	10.02	275.42	2.76	9.85	275.56	1.42	9.85
263.99	3.93	9.65	255.82	2.56	9.50	225.00	1.36	9.49
243.91	3.75	9.30	235.88	2.39	9.16	234.38	1.24	9.14
226.23	3.45	9.00	217.51	2.29	8.86	214.99	1.23	8.82
208.87	3.21	8.72	199.68	2.15	8.57	196.82	1.10	8.53
192.34	2.99	8.45	182.94	1.97	8.31	179.14	1.00	8.25
176.41	2.80	8.21	166.21	1.86	8.05	161.44	0.96	7.98
161.17	2.59	7.97	150.22	1.70	7.80	144.43	0.86	7.72
146.41	2.38	7.75	134.50	1.52	7.57	127.28	0.81	7.46
131.77	2.17	7.52	118.64	1.39	7.33	110.68	0.71	7.20
117.35	1.96	7.31	103.19	1.21	7.09	93.87	0.61	6.95
103.13	1.73	7.09	87.61	1.05	6.85	77.33	0.51	6.68
88.63	1.51	6.86	72.03	0.88	6.60	60.66	0.42	6.41
74.21	1.26	6.63	56.24	0.73	6.33	44.06	0.31	6.11
59.31	1.05	6.38	40.25	0.56	6.04	27.33	0.20	5.76
44.27	0.80	6.11	23.99	0.39	5.69	10.51	0.06	5.29
28.62	0.58	5.79	7.66	0.17	5.18			
12.90	0.28	5.38						

NOMENCLATURE

N_k = amount adsorbed at P_k
P_i = pressure in low pressure system
V = volume of low pressure system
P_k = pressure in adsorption cell
$\bar{V}$ = dead space volume
Z_i = compressibility factor at P_i
Z_k = compressibility factor at P_k
R = gas constant
T = adsorption temperature

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Some Derivatives of 2-(*p*-Aminoaryl)-2-arylethylamines

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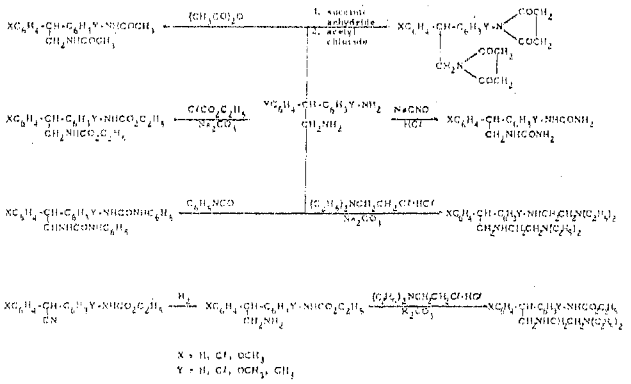
The *N,N'*-diacetyl, *N,N'*-disuccinyl, *N,N'*-dicarbethoxy, *N,N'*-dicarbamyl, *N,N'*-bis-(phenylcarbamyl), *N,N'*-bis(2'-diethylaminoethyl), *N'*-carbethoxy, and *N'*-carbethoxy-*N*-(2''-diethylaminoethyl) derivatives of some 2-(*p*-aminoaryl)-2-arylethylamines are described.

THE compounds reported here were prepared as part of an investigation of the chemical behavior of the 2-(*p*-aminoaryl)-2-arylethylamines and for submission to physiological testing programs. The diarylethylamines employed have been previously described (*2*).

The *N,N'*-diacetyl derivatives of the 2-(*p*-aminoaryl)-2-arylethylamines were prepared by the reaction of these amines with acetic anhydride following a procedure similar to that of Vogel (*6*). The corresponding *N,N'*-disuccinyl substituted compounds were obtained by treating the amines with succinic anhydride, followed by treatment with acetyl chloride according to the methods of Fieser (*4*). The *N,N'*-dicarbethoxy analogs were synthesized by way of the procedure of Damschroeder and Shriner (*1*). The *N,N'*-bis(phenylcarbamyl) derivatives were prepared by adding two molar equivalents of phenyl isocyanate to solutions containing one molar equivalents of the 2-(*p*-aminoaryl)-2-arylethylamines in tetrahydrofuran. These reaction mixtures were heated at reflux for one-half hour and then allowed to cool, whereupon the products precipitated. The *N,N'*-bis(2''-diethylaminoethyl) substituted amines were obtained by the reaction of the amines with 2-diethylaminoethyl chloride hydrochloride and sodium carbonate according to the method of Peak and Watkins (*5*). They were isolated and purified as salts.

The 2-(*p*-*N*-carbethoxyaminoaryl)-2-arylethylamines were prepared by the Raney nickel catalyzed reduction of the corresponding *p*-*N*- carbethoxyaminoarylarylacetonitriles, previously described (*3*), in tetrahydrofuran with an initial hydrogen pressure of about 1000 p.s.i.g. in a suitable reaction vessel with rocking, and heated at about 50° to 80° C. for 1 to 2 hours. Some of the products were isolated and purified as salts. The 2-(*p*-*N*-carbethoxyaminoaryl)-2-arylethylamines were then converted to the 2-(*p*-*N*-carbethoxyaminoaryl) -2- aryl -*N*- (2'-diethylaminoethyl)ethylamines using 2-diethylaminoethyl chloride hydrochloride and potassium carbonate following the procedure of Peak and Watkins (*5*). These products were isolated and purified as salts.

The transformations of this investigation can be pictured by the following reaction schemes. Table I lists the compounds which were isolated and identified. Structures of the products were assigned on the basis of elemental analyses, infrared spectral data, and similarity in the reactions involved to known transformations.



The infrared spectra were obtained using solutions of the derivatives in chloroform of those compounds which were reasonably soluble in chloroform. For the other derivatives, the spectra were obtained using mulls in Nujol or potassium bromide disks. As for compounds initially isolated as oils, infrared spectra were obtained both for the oils and the purified salts. All derivatives showed at least some modification of the amino absorption bands in the 2.8- to 3.0-micron region in comparison with the spectra of the underivatized compounds. Typical carbonyl absorption bands were in the 5.6- to 6.1-micron region of the spectra of all derivatives except the *N,N'*-bis(2''-diethylaminoethyl) derivatives. However, the salts of the latter did show typical carbonyl peaks. In addition, all salts showed characteristic broad bands in the 3.0- to 4.0-micron region. The *N,N'*-disuccinyl compounds showed no nitrogen to hydrogen absorption in the 2.8- to 3.0-micron region.