Table II. Interfacial Tensions of the 1-Alkene–Water Systems—Thermodynamic Properties of the Interfacial Region

t, ° C.	γ_i	$-(d\gamma_i/dt)$	L_i	U_i
		1-Tridecene		
25	49.29±0.13	0.0521	15.53	64.82
35	48.66±0.13	0.0723	22.29	70.95
45	47.92±0.13	0.0924	29.40	77.32
55	46.82±0.14	0.1126	36.95	83.77
65	45.59±0.14	0.1327	44.87	90.46
		1-Tetradecene		
25	47.77±0.13	0.0107	3.19	50.96
35	47.64±0.13	0.0151	4.65	52.29
45	47.47±0.13	0.0195	6.20	53.67
55	47.25±0.13	0.0239	7.84	55.09
65	46.99±0.13	0.0283	9.57	56.56
		1-Pentadecene		
25	47.66±0.13	0.0223	6.65	54.31
35	47.38±0.13	0.0331	10.20	57.58
45	46.99±0.13	0.0438	13.94	60.93
55	46.50±0.14	0.0546	17.92	64.42
65	45.90±0.14	0.0654	22.12	68.02
		1-Hexadecene		
25	47.51±0.13	0.0130	3.88	51.39
35	47.29±0.13	0.0296	9.12	56.41
45	46.92±0.13	0.0461	14.67	61.59
55	46.37±0.13	0.0627	20.58	66.95
65	45.66±0.13	0.0792	26.78	72.44

Table II shows that the entropy and the latent heats of the interfacial region increase with the temperature. Changes in this direction are to be expected. The increasing entropy reflects the increasing disorder within the interfacial region. If the theory underlying the latent heat of formation of unit area of liquid-gas interface (2) is accepted as valid for the dineric interface, then the given quantity of heat for each given temperature may be regarded as that required to extend the interfacial region by unit area, and this quantity is proportional to the temperature.

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RECEIVED for review September 19, 1966. Accepted February 3, 1967. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Adsorption of Carbon Dioxide and Nitrogen on Charcoal at 30° to 50° C.

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Isotherms for carbon dioxide and nitrogen on metal impregnated and nonimpregnated charcoal were obtained in the temperature range of 30° to 50° C. Isosteric heats of adsorption were also determined. Carbon dioxide was more favorably adsorbed in all cases. The more favorable adsorbent for carbon dioxide was shown to be a function of temperature while the nonimpregnated charcoal was more favorable for nitrogen over the range studied.

MOST DATA which have been reported on the physical adsorption of carbon dioxide and nitrogen on various charcoals are at temperatures of 20° C. and lower. Many of these data have been summarized and compared (*5*). Recently, Major, Sollami, and Kammermeyer (*4*) reported adsorption data for CO_2 at 1 atm. on 15 different carbons at 23° to 27° C. Charcoals used in the present work are relatively new products of Pittsburgh Coke and Chemical Co. for which no CO_2 or N_2 data have been reported previously at any temperature.

EXPERIMENTAL

Materials.

Charcoal type	BPL	ASC (metal impregnated BPL)
Surface area	1050–1150 m.^{2}/gram	800–850 m.^{2}/gram
Apparent Density	0.50 grams/cc.	0.58–0.60 grams/cc.
Mesh	12 × 30	12 × 30
Carbon Dioxide	99.995% pure	
Nitrogen	99.4% pure (0.6% O_2)	

Equipment. A static gravimetric adsorption apparatus of the McBain and Bakr type (*3*) with a 30-cm. adsorption chamber was used. The weight of gas adsorbed was measured by the extension of calibrated quartz spring. Pressures were measured by mercury manometers. All height or distance measurements were made using 40-cm. Eberbach cathetometers. Temperature was maintained by circulating heated air outside the adsorption chamber located within an insulated container. Heat was furnished by a hot air blower and was controlled to approximately ±½° C. with a bimetallic control switch. Details of the experimental unit are given in (*5*).

Procedure. Charcoal adsorbent was placed in a small sample holder suspended from the quartz spring. The surface of the charcoal was evacuated by applying a vacuum $\ll 1$ mm. of Hg while heating the exterior of the adsorption chamber to an excess of 200° C. by means of Electro-thermal heating tapes. This process was continued for more than an hour; tapes were removed and the chamber was allowed to come to the desired temperature level. Prior to making equilibrium measurements, the charcoal was contacted with the gas and the evacuation procedure repeated several times. The adsorbate then was admitted to the adsorption cham-

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ber. When equilibrium was established—no further change in chamber pressure or spring extension—the data were recorded and comprised the first point of the isotherm. Subsequent points were obtained by further addition of gas. All data were checked by duplicate runs with separate charcoal samples.

RESULTS

The adsorption equilibrium data are presented in Tables I and II. Data for the 30° and 40° C. isotherms also are plotted in Figures 1 and 2. The 50° C. isotherms for the CO_2 have been omitted for the sake of clarity.

The initial concavity of the isothermal plots may be attributed to strong site adsorption upon first contact between charcoal and gas as predicted by other experimenters (*1*). The inherent heterogeneity of the surface potential for adsorption implies that some adsorption sites will more readily attract adsorbate, filling immediately upon gas contact at relatively low equilibrium pressures. At higher surface coverages potential adsorption sites show more equal attractive forces and a linear relationship is followed.

Table I. Carbon Dioxide Adsorption

g/m (Gas Adsorbed/ G. Charcoal)	*P*, Cm. Hg	*g/m* (Gas Adsorbed/ G. Charcoal)	*P*, Cm. Hg
BPL 30° C.		BPL 40° C.	
0.0223	14.15	0.0199	13.75
0.0332	26.43	0.0352	30.00
0.0501	46.10	0.0425	41.30
0.0573	56.80	0.0515	55.40
0.0650	66.00	0.0596	69.60
0.0259	17.10	0.0117	6.15
0.0056	2.90	0.0262	20.00
0.0111	5.35	0.0325	26.50
0.0148	7.90	0.0407	38.80
0.0380	32.80	0.0470	48.10
0.0226	14.60		
0.0389	33.35	BPL 50° C.	
0.0551	52.75	0.0099	6.00
BPL 30° C.[a]		0.0190	16.10
0.0535	48.50	0.0289	25.70
0.0480	40.70	0.0388	41.10
0.0425	32.50	0.0497	60.50
0.0312	20.00	0.0570	76.20
0.0220	10.55	0.0037	2.50
0.0135	5.25	0.0144	10.90
		0.0442	50.60
		0.0115	8.30
		0.0253	21.20
		0.0343	34.20
ASC 30° C.		ASC 40° C.	
0.0268	17.05	0.0210	17.25
0.0688	67.30	0.0344	33.95
0.0193	11.00	0.0428	50.10
0.0385	28.20	0.0520	67.60
0.0587	53.10	0.0134	8.55
0.0101	4.00	0.0394	40.95
0.0285	16.40	0.0067	4.50
0.0453	35.25	0.0202	14.15
0.0117	4.40	0.0252	21.45
0.0218	10.40	0.0352	35.40
0.0638	60.20	0.0403	44.70
0.0151	7.15	0.0461	55.90
0.0436	36.60	0.0235	17.80
		0.0319	29.15
ASC 50° C.		ASC 50° C.	
0.0042	3.25	0.0396	58.40
0.0115	9.45	0.0438	70.55
0.0188	18.80	0.0083	7.05
0.0240	26.30	0.0167	17.05
0.0281	34.50	0.0313	40.05
0.0354	47.40	0.0427	66.45

[a] Previously uncontacted.

Table II. Nitrogen Adsorption

g/m (Gas Adsorbed/ G. Charcoal)	*P*, Cm. Hg	*g/m* (Gas Adsorbed/ G. Charcoal)	*P*, Cm. Hg
BPL 30° C.		ASC 30° C.	
0.0037	20.05	0.0025	20.10
0.0065	43.65	0.0050	52.10
0.0102	72.55	0.0067	72.35
0.0083	61.25	0.0020	16.95
0.0018	6.10	0.0042	41.10
0.0028	11.65	0.0059	62.45
0.0046	27.60	0.0017	10.75
0.0056	36.30	0.0034	29.85
0.0074	55.70	0.0067	72.90
0.0093	71.30		
BPL 40° C.		ASC 40° C.	
0.0018	10.10	0.0034	47.85
0.0036	27.45	0.0042	72.20
0.0027	17.60	0.0008	7.30
0.0045	43.80	0.0017	13.95
0.0063	74.00	0.0025	28.15
0.0009	4.60		
0.0054	61.85		

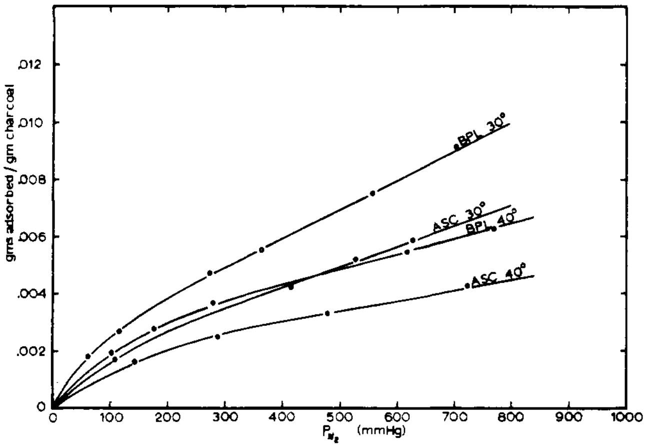

Figure 1. Equilibrium isotherms for N_2 on activated carbon

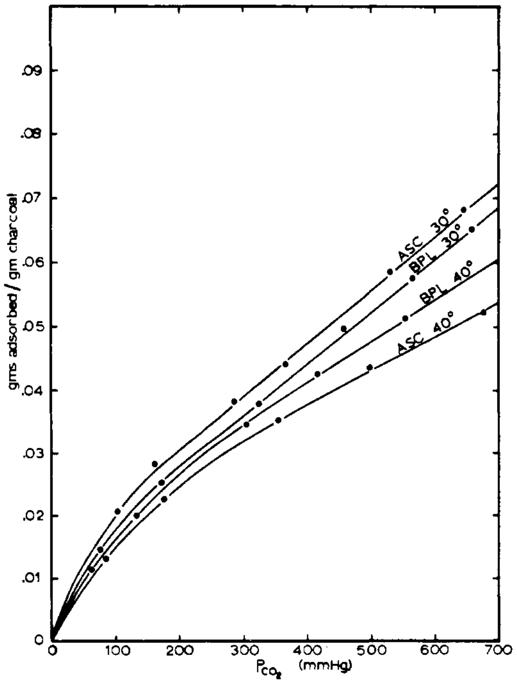

Figure 2. Equilibrium isotherms for CO_2 on activated carbon

Isosteric heats of adsorption were calculated from the measured isotherms and are given in Table III. Calculations were made from the following equation which is based upon the Clausius-Clapeyron form.

$$\Delta H_{is} = \left(\frac{T_1 T_2}{T_2 - T_1} \right) R \ln \left(\frac{P_2}{P_1} \right) \qquad (1)$$

Constancy of the isosteric heat over the range investigated is demonstrated for several isosteres in Figure 3 where the slope of the line is proportional to the heat of adsorption.

DISCUSSION

The general shape of the pure gas isotherms is identical; all show initial curvature, concave to the pressure axis, followed by a linear portion. Data from Figure 3 and similar plots were used to extrapolate to 25° C. and a CO_2 pressure of 1 atm. for comparison with the data of Major, Sollami, and Kammermeyer (*4*). The charcoals used in that study showed a range of adsorption ability from 0.060 to 0.106 grams of CO_2 per gram of charcoal. Data of the present work give 0.08 and 0.09 gram of CO_2 per gram of charcoal for ASC and BPL, respectively.

BPL charcoal proved to be the more effective when adsorbing N_2 for both 30° and 40° C. isotherms as shown in Figure 1. The ratio of adsorbing ability of the two charcoals is roughly the same as the ratio of the reported surface areas.

For the adsorption of CO_2 such was not the case. Figure 2 shows more favorable adsorption by the metal impregnated ASC at 30° C., while BPL exhibited the more favorable adsorption at 40° and 50° C. Owing to the presence of metal impregnates in the ASC type charcoal, Van der Waal forces are determined by different molecules than are normally present in the charcoal. The effect of temperature in the adsorption of gases on ASC and BPL may differ along with the heats of adsorption. Any effects such as this would be more pronounced on the polar CO_2 molecule than on the more nearly symmetric N_2 molecule. Table III shows the same order of magnitude for the heat of adsorption for N_2 on the two charcoals. Figure 3 and Table III show significant differences for CO_2 on these charcoals. The high heat of adsorption shown for the low surface coverage is in agreement with observation of Grahm (*2*).

Table III. Isosteric Heats of Adsorption

g/m (Gas Adsorbed/ G. Charcoal)	Charcoal Type	$-\Delta H_{is}$ Kcal./G. Mole
	Carbon Dioxide	
0.02	BPL	3.04
0.03	BPL	1.04
0.04	BPL	1.55
0.05	BPL	2.43
0.06	BPL	2.73
0.02	ASC	7.62
0.03	ASC	5.90
0.04	ASC	6.47
0.05	ASC	7.02
	Nitrogen	
0.001	BPL	10.20
0.002	BPL	8.49
0.003	BPL	8.86
0.004	BPL	9.34
0.005	BPL	10.22
0.002	ASC	7.30
0.003	ASC	9.54
0.004	ASC	10.99

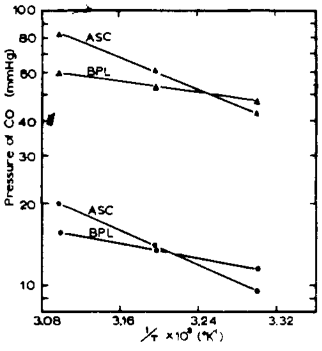

Figure 3. Isosteres of CO_2

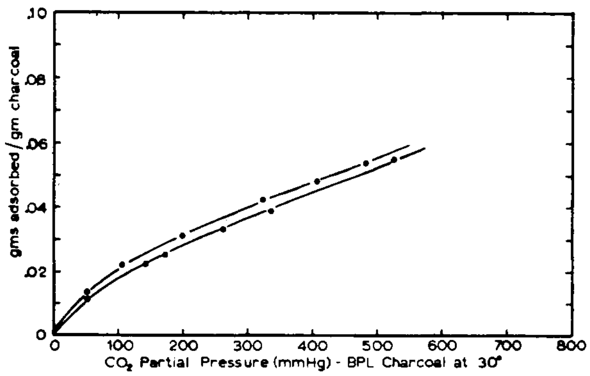

Figure 4. Effect of previous contact on adsorptive power of BPL

○ With previously contacted charcoal (normal run)

● With charcoal not previously used for CO_2

All but one set of data for this work were taken using charcoal which purposely had been contacted by the adsorbate then degassed. Uncontacted charcoal shows greater adsorptive power than it does for the second and succeeding contacts. Data for second and succeeding contacts were identical and reproducible. Longer evacuation time and higher evacuation temperatures did not alter this phenomenon. The difference exhibited by uncontacted charcoal can be seen in Table I and Figure 4. This adsorption hysteresis has been discussed by Treybal (*7*), among others.

Using the concept of the adsorbate existing as a two-dimensional gas in the form of spherical molecules, the surface area covered for a given adsorption may be estimated (*6*). For this work the maximum coverage was 13%.

NOMENCLATURE

g = grams of adsorbate
m = grams of adsorbent
P = equilibrium pressure, cm. Hg
R = gas constant, cal./mole ° K.
T = equilibrium temperature, ° K.
ΔH_{is} = isosteric heat of adsorption, kcal./g. mole

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RECEIVED for review September 22, 1966. Accepted January 21, 1967.