

Adsorption of Carbon Dioxide, Acetylene, Ethane, and Propylene on Charcoal at Near Room Temperatures

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The adsorption equilibria for acetylene, ethane, and propylene on an activated charcoal were obtained. Isotherms were measured for the pure gases in the temperature range 30° to 50° C. and pressures up to 1 atm. These adsorption isotherms have been correlated by a modification of the Polanyi adsorption potential theory and by a semitheoretical relationship proposed by Koble and Corrigan. A similar correlation for adsorption data obtained for carbon dioxide, on the same activated charcoal with the same experimental conditions of temperature and pressure, is included.

THE DATA PRESENTED were obtained as a part of a continuing study of adsorption equilibria on charcoal. Data used for the correlation of CO₂ adsorption obtained using the same apparatus and charcoal have been reported by Meredith and Plank (8).

APPARATUS AND PROCEDURE

Materials. The charcoal was a commercial grade bituminous coal-based activated charcoal, designated as BPL by the Pittsburgh Activated Carbon Co. The charcoal size was 12 × 30 mesh, possessing a surface area at 1050 to 1150 sq. meters per gram and an apparent density of 0.50 gram per cc. Adsorption isotherms for nitrogen from Grant and Manes (2) and Meredith and Plank (8), including the one at nitrogen's normal boiling point, are presented in Figure 1 to characterize this charcoal better.

All gases used were better than 99% pure.

Equipment. A static gravimetric adsorption apparatus was used with a McBain quartz spring in a 30.0-cm. long glass adsorption chamber. The weight of adsorbed gas was determined by suspending the charcoal in a pan from the spring and noting changes in the spring deflection, measured by a 40.0-cm. scale Eberbach cathetometer. Equilibrium pressures above the charcoal were measured by mercury manometers. Experimental measurements were accurate to ±0.5 mm. of Hg and ±0.00024 gram of gas adsorbed per gram of charcoal. Charcoal sample size was approxi-

mately 0.25 gram. Experimental temperatures were maintained constant by circulating heated air within the insulated container surrounding the adsorption chamber. Heat was furnished by a hot air blower controlled to approximately ±0.5° C. by a bimetallic control switch. Details are given by Laukhuf (6).

Procedure. The charcoal sample was placed in a small pan suspended from the quartz spring. Prior to making equilibrium measurements for a particular gas-solid system, the charcoal was twice brought in contact with the gas to be investigated. To prepare the charcoal surface for an experimental run, a vacuum was applied to the adsorption chamber while heating the exterior of the chamber to above 200° C. by electrothermal heating tapes. This produced pressures in the chamber of less than 0.05 mm. of mercury as measured by a McLeod gage. The data were reproducible. The potential adsorbate was admitted to the adsorption chamber. After half an hour there were no further changes in either chamber pressure or spring extension.

The initial data point of an isotherm was recorded at times in excess of one-half hour. Additional adsorbate was then admitted to the chamber and allowed to equilibrate. This procedure was continued until the entire isotherm had been determined. Check runs for each isotherm made subsequent to degassing established the reproducibility of the data.

RESULTS AND DISCUSSION

Carbon dioxide equilibrium data obtained using the same apparatus and charcoal as those used for acetylene, ethane, and propylene have been tabulated and plotted (8). Acetylene, ethane, and propylene equilibrium data are presented in Tables I, II, and III and shown in Figures 2,

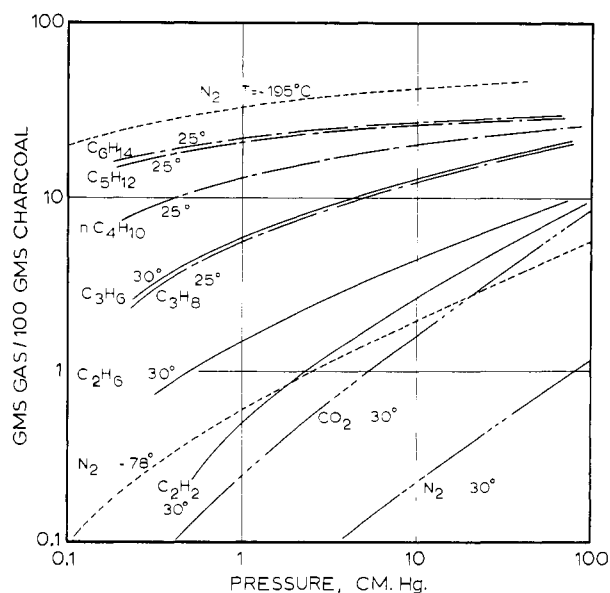


Figure 1. BPL charcoal adsorption characteristics

— New data - - - (2) - · - (3) · · · (8)

Table I. Acetylene Adsorption

30° C.		40° C.		50° C.	
Pressure, cm. Hg	G. adsorbed/g. charcoal	Pressure, cm. Hg	G. adsorbed/g. charcoal	Pressure, cm. Hg	G. adsorbed/g. charcoal
10.15	0.0254	8.10	0.0191	7.85	0.0149
20.00	0.0383	17.80	0.0318	17.60	0.0257
29.50	0.0510	28.40	0.0425	27.60	0.0361
39.95	0.0595	39.40	0.0530	37.65	0.0446
50.35	0.0680	50.90	0.0615	47.90	0.0510
61.05	0.0765	63.95	0.0721	58.55	0.0595
75.85	0.0849	75.10	0.0785	67.40	0.0658
5.70	0.0192	8.60	0.0191	76.90	0.0722
14.61	0.0340	18.50	0.0318	7.70	0.0149
25.40	0.0466	31.10	0.0446	15.40	0.0234
35.20	0.0552	41.00	0.0541	25.45	0.0340
45.95	0.0636	52.95	0.0647	35.55	0.0435
60.30	0.0764	68.20	0.0743	54.60	0.0573
		75.65	0.0796	74.00	0.0722

3, and 4 in the familiar isothermal form. The data at 30°C. of these four gases, obtained on the same commercial grade of Pittsburgh Activated Carbon Co. charcoal (BPL) at about the same temperature, are also presented in Figure 1 along with the data of Grant and Manes (2, 3). The new curves exhibit the same general shape and relative placement as those of other hydrocarbon gases.

Figures 2, 3, and 4 are arranged in ascending order of charcoal adsorption capacity, acetylene being the least adsorbed and propylene being adsorbed to the greatest extent for all temperatures and pressures investigated. The adsorption capacity with carbon dioxide was considerably less than with acetylene. All four gases exhibit isotherms of the same general shape.

The low pressure curvature of these isotherms may be a result of the immediate filling of adsorption sites whose potential is much higher than that of other sites. As these

highly active sites are filled, the remaining ones tend to possess more equal adsorption potentials, producing the approach to linearity of the adsorption isotherm. This action is characteristic of an adsorbent possessing heterogeneous surface potential sites for adsorption, for which charcoal is noted.

As expected, Figures 2, 3, and 4 show a decrease in the amount of gas adsorbed with increasing temperature. Plots of $\ln P$ vs. $1/T$ for constant amounts adsorbed yield reasonably straight lines. Isothermic heats of adsorption may be calculated from such plots by utilizing the Clausius-Clapeyron equation. Such calculations have been made for these gas-solid systems; the results point out the heterogeneity of the adsorption potential of the charcoal surface

Table II. Ethane Adsorption

30° C.		40° C.		50° C.	
Pressure, cm. Hg	G. adsorbed/ g. charcoal	Pressure, cm. Hg	G. adsorbed/ g. charcoal	Pressure, cm. Hg	G. adsorbed/ g. charcoal
6.60	0.0340	3.65	0.0230	3.41	0.0170
15.75	0.0520	10.95	0.0400	9.25	0.0290
24.90	0.0620	18.60	0.0510	18.05	0.0420
33.55	0.0720	27.15	0.0610	26.55	0.0490
44.00	0.0820	37.15	0.0680	35.80	0.0580
54.50	0.0890	46.15	0.0760	44.45	0.0630
66.30	0.0960	57.75	0.0830	53.00	0.0680
77.80	0.1010	66.60	0.0880	66.30	0.0720
3.15	0.0260	77.90	0.0920	76.50	0.0760
9.45	0.0430	5.25	0.0260	5.30	0.0220
17.30	0.0560	13.40	0.0440	16.15	0.0380
26.15	0.0670	23.50	0.0580	26.70	0.0500
36.25	0.0760	33.05	0.0670	37.20	0.0580
48.20	0.0840	42.25	0.0740	49.30	0.0670
57.75	0.0910	55.55	0.0820	57.45	0.0700
76.05	0.1000	66.20	0.0880	66.60	0.0720
		77.05	0.0910	75.65	0.0760

Table III. Propylene Adsorption

30° C.		40° C.		50° C.	
Pressure, cm. Hg	G. adsorbed/ g. charcoal	Pressure, cm. Hg	G. adsorbed/ g. charcoal	Pressure, cm. Hg	G. adsorbed/ g. charcoal
5.75	0.0992	3.20	0.0708	1.15	0.0425
12.35	0.1275	10.20	0.1105	5.35	0.0794
18.80	0.1445	16.45	0.1275	9.95	0.0992
25.10	0.1558	28.15	0.1473	15.50	0.1190
37.35	0.1700	38.95	0.1589	25.50	0.1378
47.70	0.1785	57.85	0.1785	35.80	0.1502
58.30	0.1870	73.35	0.1845	46.35	0.1614
68.30	0.1927	1.30	0.0454	56.65	0.1670
73.45	0.1983	3.40	0.0794	66.30	0.1730
0.85	0.0510	11.60	0.1162	76.05	0.1785
3.05	0.0822	20.05	0.1388		
6.30	0.1048	31.75	0.1560		
35.70	0.1728	42.50	0.1673		
57.50	0.1870	61.65	0.1755		
75.45	0.1983	67.95	0.1845		
85.10	0.2040	77.70	0.1870		
		1.10	0.0481		
		3.10	0.0765		
		7.30	0.1062		
		14.60	0.1320		
		20.85	0.1431		
		30.05	0.1560		
		40.90	0.1670		
		50.80	0.1745		
		60.65	0.1815		
		71.10	0.1885		

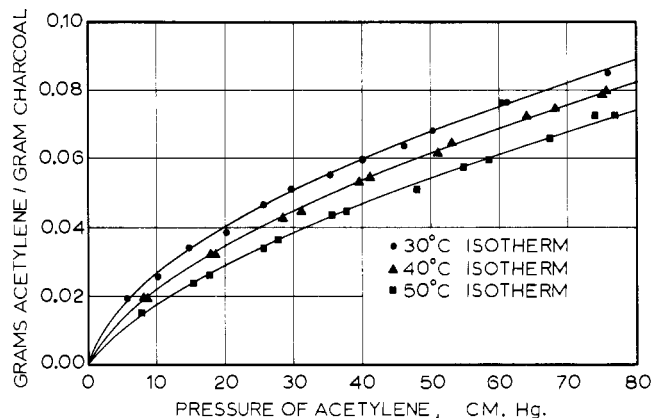


Figure 2. Pure gas data for acetylene on BPL

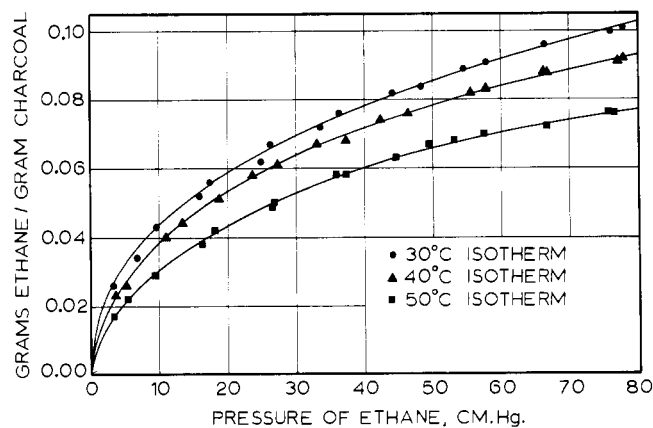


Figure 3. Pure gas data for ethane on BPL

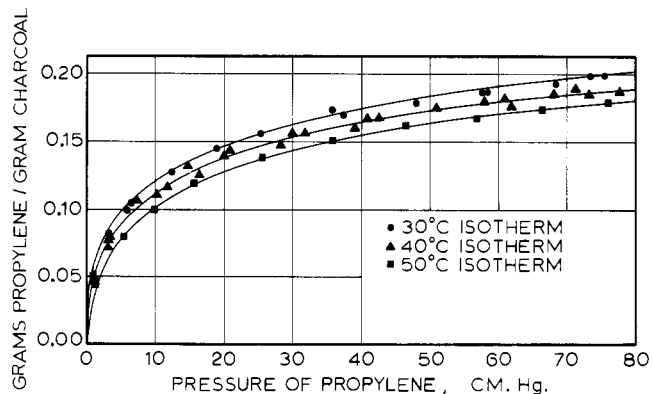


Figure 4. Pure gas data for propylene on BPL

(4, 6). For very small amounts adsorbed, the calculated isosteric heats of adsorption are higher than for larger amounts. Increasing the surface coverage decreases the heat of adsorption, emphasizing the curvature and approach to linearity of the isotherms.

The data in this experimental work have been compared with the isotherm relationships proposed by Freundlich (9), Langmuir (5), Sips (9), Koble and Corrigan (4), and Polanyi (1). The Polanyi correlation, using the modification suggested by Cook and Basmadjian (1), compares very favorably with the acetylene, ethane, and propylene data. The Koble and Corrigan equation produces an excellent representation for these three gases in addition to carbon dioxide (8). The other expressions represented the data only over very limited ranges.

The Polanyi correlation, using the modification suggested by Cook and Basmadjian (1), produces a curve of the volume of adsorbate adsorbed as a saturated liquid at the adsorption experimental conditions of temperature and pressure *vs.* $RT/V' \ln P_s/P$.

Cook and Basmadjian (1) evaluate V' in the following way. If the adsorption temperature is below the normal boiling point of the gas in question, V' is the molar volume of the gas as a saturated liquid at the adsorption temperature. If, however, the adsorption temperature is above the normal boiling point as in the present case, the molar volume should be evaluated from a straight line drawn tangent to a plot of the logarithm of the molar volume of the saturated liquid in equilibrium with its vapor *vs.* the logarithm of the absolute temperature, drawn tangent at the normal boiling point of the gas and extrapolated to the desired temperature.

Several other methods for evaluating V' were investigated with the data presented here, but the Cook and Basmadjian (1) evaluation produced the best correlation (Figure 5). Both ethane and propylene at 30°, 40°, and 50° C. formed

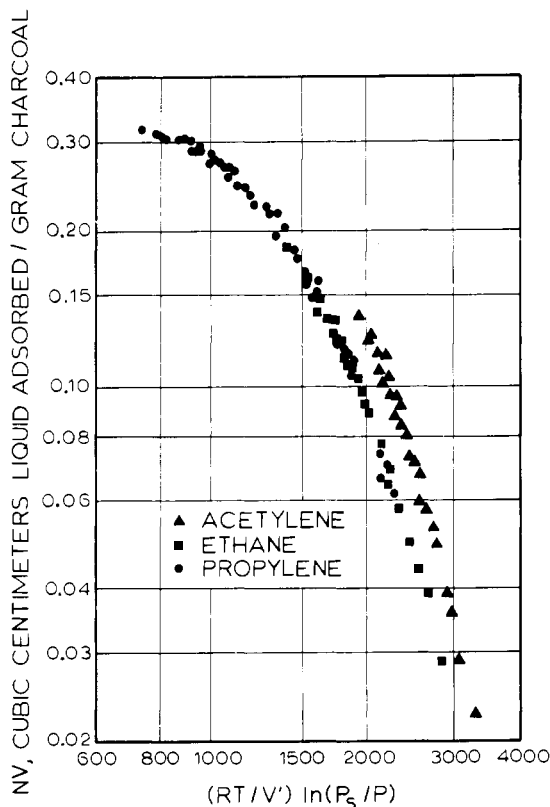


Figure 5. Polanyi correlation using Cook's evaluation

a single characteristic curve for this charcoal; acetylene forms a separate curve. This has been noted by others (7).

The semitheoretical equation proposed by Koble and Corrigan (4) was satisfied by the acetylene, ethane, and propylene as well as the carbon dioxide (8) data. As presented, the equation in the general form is

$$\theta = \frac{KP^n}{1 + KP^n} \quad (1)$$

where θ is the fraction of the surface covered by the adsorbed gas, assuming a monomolecular layer as 100% coverage.

To arrive at this equation, it was assumed that dissociation is the mechanism of adsorption. If this mechanism is correct, then according to the derivation (4), the exponent, n , should be temperature-independent for a given gas-solid system. The adsorption data for carbon dioxide, acetylene, ethane, and propylene on activated charcoal were compared with Equation 1. By using a least squares procedure, the exponent was determined for each experimental isotherm. At all three temperatures investigated for a particular gas-solid system, the exponents were essentially equal, which is compatible with the derivation.

Therefore by using all data at all three temperatures and the least squares procedure, a single exponent was obtained for each gas-solid system (Table IV).

The value of n for propylene compares very favorably with the value of 0.569 determined by Koble and Corrigan (4) for the adsorption of propylene on a very similar activated charcoal.

Using the exponents presented in Table IV, K was then evaluated for each isotherm (Table V).

Instead of figures comparing this equation with the experimental data for each gas-solid system, only the acetylene comparison is shown (Figure 6), the poorest of the four systems. The others show even less deviation. The isotherms drawn through the experimental data in Figure 6 were calculated using Equation 1, the exponents from Table IV, the constants from Table V, and the conversions listed in Table VI. These conversions represent the amount of gas required for one complete monolayer adsorbed or 100% surface coverage. The gas molecules were assumed to be spherical, and the area covered by one such molecule was determined.

Table IV. Exponents for Koble-Corrigan Equation

Carbon dioxide	0.779
Acetylene	0.763
Ethane	0.585
Propylene	0.566

Table V. Constants for Koble-Corrigan Equation

Gas	Temp., ° C.	K
Carbon dioxide	30	0.004535
	40	0.004211
	50	0.003656
Acetylene	30	0.018975
	40	0.01622
	50	0.01362
Ethane	30	0.05928
	40	0.05131
	50	0.03953
Propylene	30	0.2176
	40	0.1861
	50	0.1511

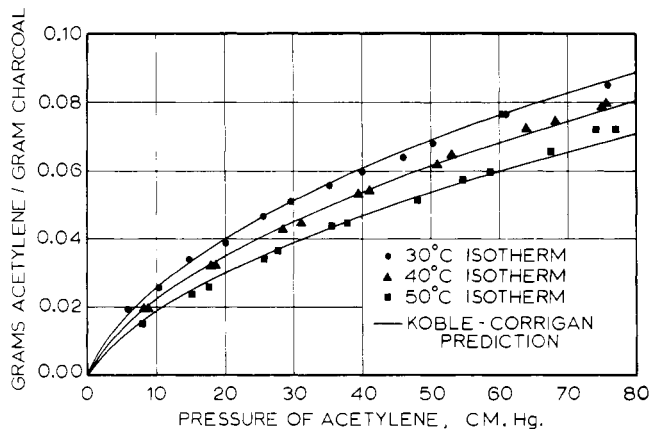


Figure 6. Experimental data vs. calculated isotherms

Table VI. Grams of Pure Gas per Gram of BPL Charcoal for 100% Surface Coverage

Gas	Gram Gas/Gram Charcoal
Carbon dioxide	0.619
Acetylene	0.254
Ethane	0.234
Propylene	0.276

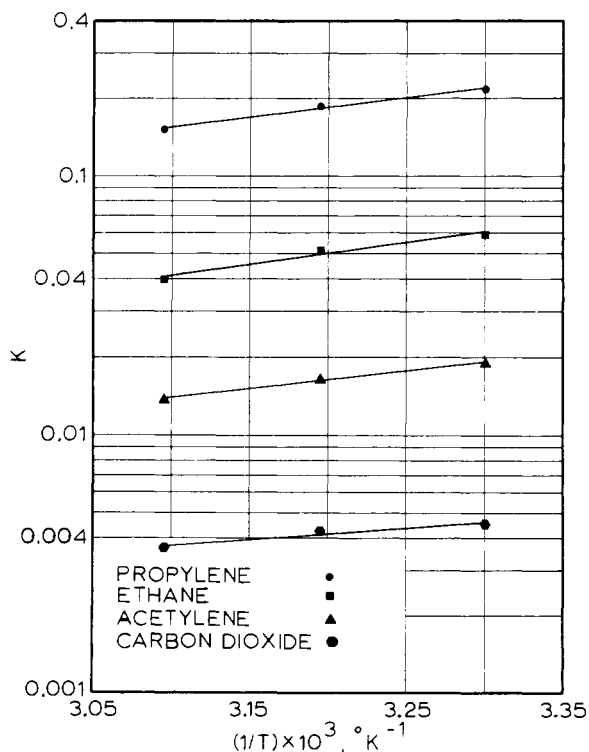


Figure 7. $\ln K$ vs. $1/T$

According to Koble and Corrigan (4), there should be a relationship between the constant, K , and temperature. Many trials were made; the best relationship is obtained when plotted as $\ln K$ vs. $1/T$, where T is the absolute temperature (Figure 7).

CONCLUSIONS

The experimental data for acetylene, ethane, and propylene on activated charcoal form reproducible isotherms. All isotherms have the same general shape, with initial curvature concave to the pressure axis followed by an approach to linearity.

The charcoal has the least adsorptive capacity for carbon dioxide and the largest capacity for propylene for the systems investigated.

The experimental data of acetylene, ethane, and propylene produce an acceptable correlation when plotted according to the Polanyi potential theory and using the modification suggested by Cook and Basmadjian. Ethane and propylene form a single temperature-independent curve, while acetylene forms a second temperature-independent curve.

The adsorption data for all four gases show excellent representation by the equation proposed by Koble and Corrigan. A single temperature-independent exponent, n , was obtained for each gas-solid system. The constant, K , in the equation when plotted as $\ln K$ vs. $1/T$, produces straight lines which allow the prediction of isotherms at temperatures other than those studied.

NOMENCLATURE

- K, n = constants in Koble-Corrigan equation
- N = number of moles adsorbed
- P = adsorption pressure, cm. of Hg
- P_s = saturated liquid vapor pressure of material being adsorbed at adsorption temperature, cm. of Hg
- R = gas law constant
- T = absolute temperature, °K.
- V' = molar volume of material adsorbed, cc. per mole
- θ = fraction of surface covered by adsorbed gas

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RECEIVED for review January 24, 1968. Accepted July 26, 1968.