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Adsorption of Normal Paraffins and Sulfur Compounds on Activated Carbon

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Adsorption isotherms on activated carbon were determined gravimetrically for normal C_1 and C_3-C_6 paraffins and subsequently for methyl, ethyl, and *n*-propyl mercaptans, hydrogen sulfide, carbonyl sulfide, and carbon disulfide, at pressures up to 1 atm. and from —23° to 100°C. Orthobaric liquid densities at low temperatures of some of the sulfur gases were determined pycnometrically. The adsorption data on correlation by the method of Lewis, Gilliland, Chertow, and Cadogan (*1*) gave two separate curves, one for the paraffins and one for the sulfur compounds. The results show the correlation to be useful for estimating the adsorptive capacity of chemically similar compounds from a minimum of experimental data.

The purpose of this work was to determine in detail the isotherms of individual normal paraffins on a single granular activated carbon adsorbent and, if possible, to correlate the isotherms by the method of Lewis, et al. (*1*). When isotherms of methane and *n*-butane were determined initially on a conventional volumetric adsorption apparatus and the results correlated, the *n*-butane isotherms diverged in the direction of lower capacity, in a manner similar to that previously noted by Walters (*2*). The effect observed could be explained by solubility of *n*-butane in the stopcock grease. A gravimetric adsorption apparatus with the McBain balance principle was therefore constructed; it gave consistent isotherms of methane and of propane to hexane. Subsequently for operating convenience a completely grease-free gravimetric system was constructed and used to determine the adsorption isotherms of a series of sulfur-containing compounds. The results were treated in the same fashion as the hydrocarbon data.

EXPERIMENTAL PROCEDURE

Apparatus

The McBain adsorption balance finally adopted was constructed of Pyrex pipe (adsorption chambers) and stainless steel

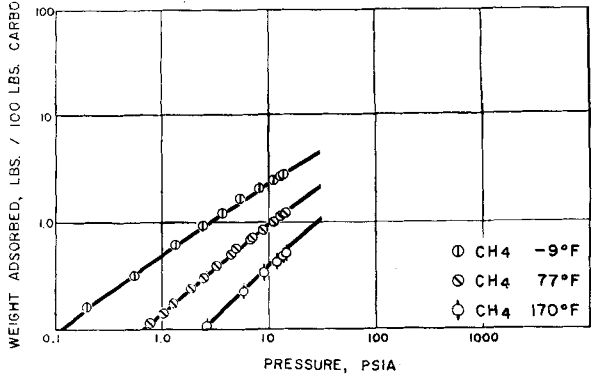

Fig. 1. Adsorption isotherms of methane on BPL (4 × 10) activated carbon.

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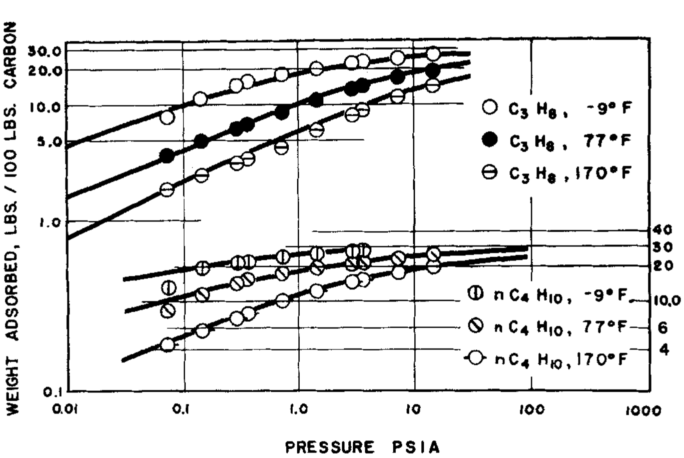

Fig. 2. Adsorption isotherms of propane and *n*-butane on BPL (4 × 10) activated carbon.

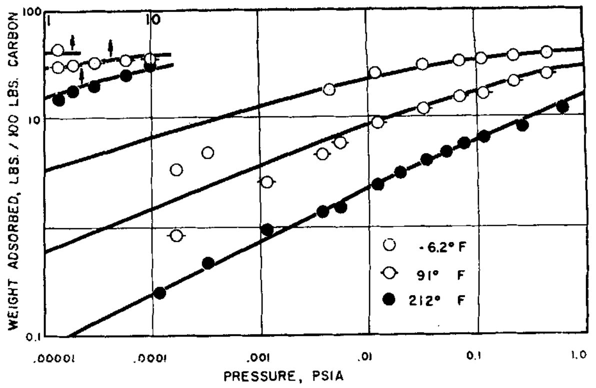

Fig. 5. Adsorption isotherms of ethyl mercaptan on BPL 2026-54 (4 × 10) activated carbon.

(tubing and valves), with Teflon gaskets and valve seats. (The original all-glass adsorption balance was similar except that stopcocks were used in place of stainless steel valves.) The Pyrex pipe adsorption chambers enclosed quartz helical springs and buckets. Spring extensions and mercury manometer pressure readings were measured with a cathetometer to 0.05 mm. Low pressures were measured by a Pirani gauge and pressures above 1 mm. Hg. by a mercury manometer. Adsorption temperatures were controlled by constant-temperature baths surrounding the adsorption chambers.

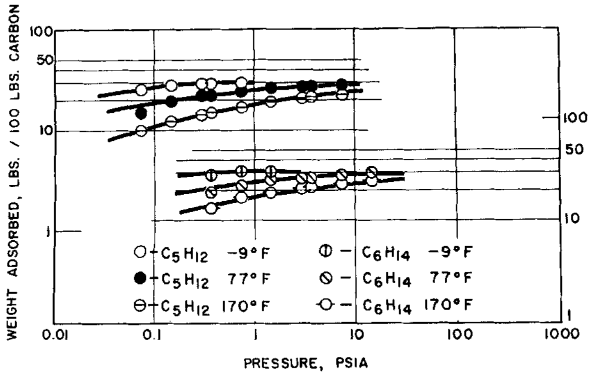

Fig. 3. Adsorption isotherms of *n*-pentane and *n*-hexane on BPL (4 × 10) activated carbon.

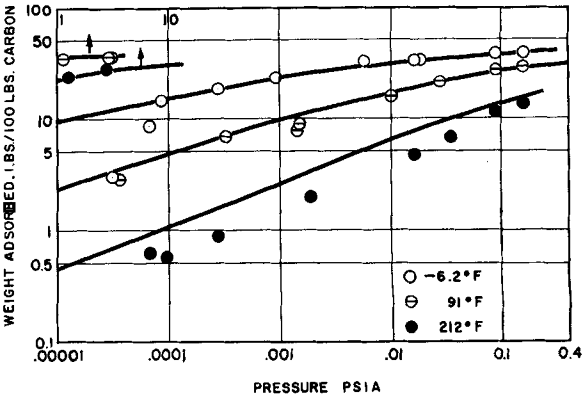

Fig. 6. Adsorption isotherms of normal propyl mercaptan on BPL 2026-54 (4 × 10) activated carbon.

Materials

Methane, instrument grade propane and *n*-butane, and pure grade *n*-pentane and *n*-hexane were used without further purification. Methane, *n*-pentane, and *n*-hexane were 99.0% minimum purity, propane and *n*-butane were 99.9% minimum purity. Purified grade hydrogen sulfide (99.5% minimum purity), carbonyl sulfide (96% minimum purity, liquid phase), and methyl mercaptan (99.0% minimum purity) were used. By gas chromatographic analysis these gases were 97.1, 96.8, and 96.9% pure respectively. Ethyl mercaptan and *n*-propyl mercaptan were analyzed as 98.7% pure by gas chromatography. The gases were condensed at —78°C. (dry ice-acetone) and evacuated to constant vapor pressure to remove noncondensables. The remaining liquid was evaporated into 5-liter gas reservoirs. The three liquids were also evacuated at dry ice-acetone temperature to constant vapor pressure and sampled directly.

Adsorbents

Some properties of the two Pittsburgh Chemical Company coal-base (4 × 10 mesh) activated carbons (designated BPL) are shown in Table I. They differed essentially only in ash content, the higher

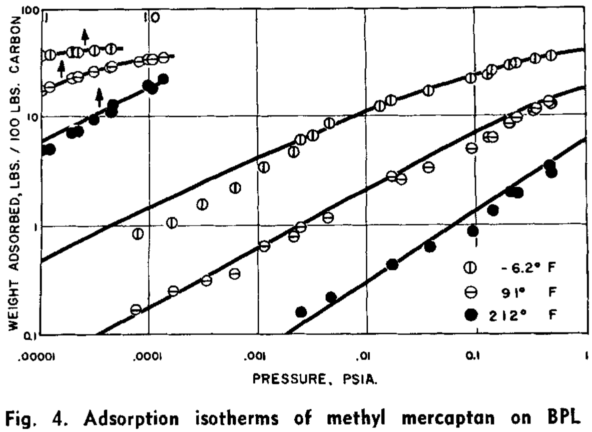

Fig. 4. Adsorption isotherms of methyl mercaptan on BPL 2026-54 (4 × 10) activated carbon.

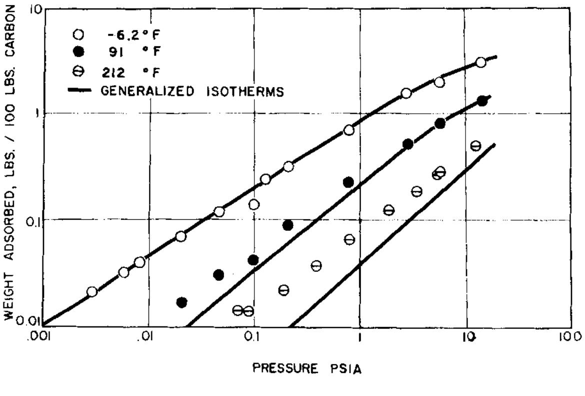

Fig. 7. Adsorption isotherms of hydrogen sulfide on BPL 2026-54 (4 × 10) activated carbon.

Table 1. Properties of BPL Carbon

	Paraffin series BPL SS no.2	Sulfur compounds BPL 2026-54
Surface area, m.^{2}/g. (BET)	1,004	1,040
Real density, g./cc.	2.178	2.163
Particle density, g./cc.	0.777	0.803
Ash, wt.-%	7.54	5.29

ash content carbon on which the hydrocarbon data were determined now being obsolete. Helium and mercury densities of the carbons were determined by displacement according to the method of Juhola (*3*). Micropore size distribution was determined by the water desorption isotherm method (*4*) and macropore size distribution by mercury porosimeter (*4*). The pore size distributions of both carbons were typical. The volume in pores of 100Å. diam. or less was 0.45 cc./g., of which 0.4 cc./g. was in pores around 18Å. diam.

Calibration

The quartz springs were calibrated with known (analytical) weights. The spring sensitivity, about 450 mm./g., was constant within 1% over the entire range; all weights were therefore determined directly as spring extensions.

For each gas the Pirani gauge was calibrated against the McLeod gauge, starting at the reservoir pressure and decreasing the pressure step-by-step. This procedure was followed to minimize fractionation of high volatile impurities from the liquid reservoir and in the case of the gases to minimize possible fractionation due to selective adsorption on the walls of the equipment.

Isotherm Determinations

The isotherms of the normal paraffins were determined at —22.6°C. (—9°F.), 25°C. (77°F.), and 76.8°C. (170°F.). The sulfur gas isotherms were determined subsequently at —21.2°C. (—6.2°F.), 32.8°C. (91°F.), and 100°C. (212°F.). The pressure range in both series was from 0 to 760 mm. Hg. The activated carbon samples (approximately 0.4 g.) were evacuated before each run to at least 0.001 mm. Hg. at 400°C. for 2 hr. Vapor was admitted to the sample from the reservoir, and equilibrium was considered to have been reached when no further change in spring extension or pressure was detected. Prior to reaching equilibrium the chamber was momentarily evacuated to remove traces of nonadsorbable impurities. Spring extension was followed as a function of pressure. Buoyancy corrections were negligible.

Physical Properties for Calculations

The correlation of the adsorption results (to be discussed later) required data on the vapor pressure, fugacity, and liquid density over a wide range of conditions. Maxwell (*5*) was the source for all of the hydrocarbon data, including extrapolated values for the saturation fugacity of methane above its critical temperature. The literature was consulted for vapor-pressure data on hydrogen sulfide (*6*), carbonyl sulfide (*7*), carbon disulfide (*6*), methyl mercaptan (*8*), ethyl mercaptan (*9*), and *n*-propyl mercaptan (*10*). Where the literature data did not quite cover the entire range of interest, log vapor pressure was linearly extrapolated against reciprocal absolute temperature. Fugacities for saturated carbonyl sulfide at 100°C. and hydrogen sulfide at 32.8° and 100°C., were calculated from van der Waals' constants (*6*) by the method of Lewis and Randall (*11*). In all other cases the fugacities of the sulfur gases could be assumed to be equal to the pressures.

The orthobaric liquid densities of hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and *n*-propyl mercaptan were determined directly at low temperatures by a pycnometric method (*12*). The pycnometer, which did not require refilling at each temperature, was in effect a volume-calibrated thermometer with bulb and graduated stem. The sulfur gases were condensed in the bulb at the lowest temperature of measurement, the thermometer was evacuated and sealed, and the liquid level in the capillary was read by cathetometer (through an unsilvered vacuum flask) as the bath temperature rose slowly. The liquid density of ethyl mercaptan was not determined since the values in the literature (*13*) for the densities of ethyl and *n*-propyl mercaptan between 0° and 23°C. were almost identical. The density of carbon disulfide was taken from the literature (*14*).

RESULTS AND CORRELATION

The adsorption isotherms of the normal paraffins are shown in Figures 1 to 3 in the familiar Freundlich log-log plot of parts by weight adsorbed (per one hundred parts of carbon) against adsorption pressure. The points are experimental; the solid lines have been recalculated from the generalized correlation, to be discussed. The adsorption isotherms of the sulfur gases are shown in Figures 4 to 9.

The correlation of Lewis et al. *(1)* is essentially a plot of the volume of the adsorbed liquid against $T/V' \ln f_s/f$, this term being proportional to the adsorption potential per unit volume where T = adsorption temperature, °K.; V' = molar volume of saturated liquid at the temperature where vapor pressure equals adsorption pressure, cc./g. mole; f = fugacity of the gas at adsorption pressure and temperature; and f_s = fugacity of saturated liquid at adsorption temperature.

In this correlation the density of the adsorbed liquid is estimated by assuming it to be equal to the density of the normal liquid at the temperature where the saturation pressure has the magnitude of the adsorption pressure. For convenience in calculating, orthobaric liquid densities were plotted against saturation pressure (or adsorption pressure in this case).

The hydrocarbon correlation is shown in Figure 10. Common logarithms have been used; points have been omitted only for lack of space. The standard deviation of the predicted value of pressure from the true value (given the volume adsorbed) is estimated at ±5% of the true value, as can be seen qualitatively from the fit of the experimental points to the calculated isotherms. This fit is of the same order of precision as that reported by Lewis, et al. *(1)*, but the adsorptive capacity is greater than that of the now obsolete

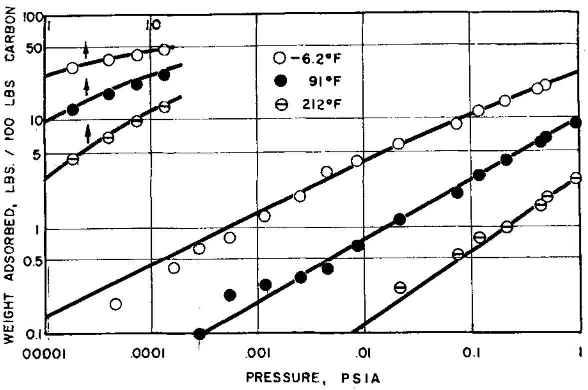

Fig. 8. Adsorption isotherms of carbonyl sulfide on BPL 2026-54 (4 × 10) activated carbon.

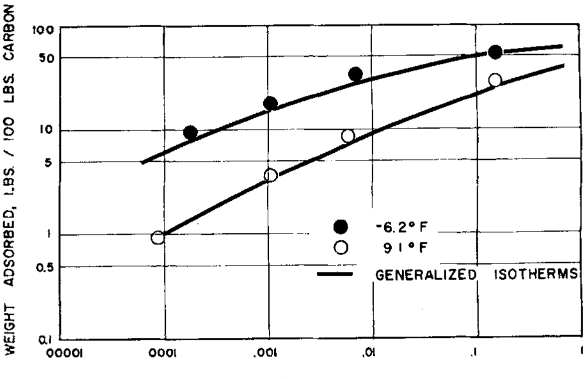

Fig. 9. Adsorption isotherms of carbon disulfide on BPL 2026-54 (4 × 10) activated carbon.

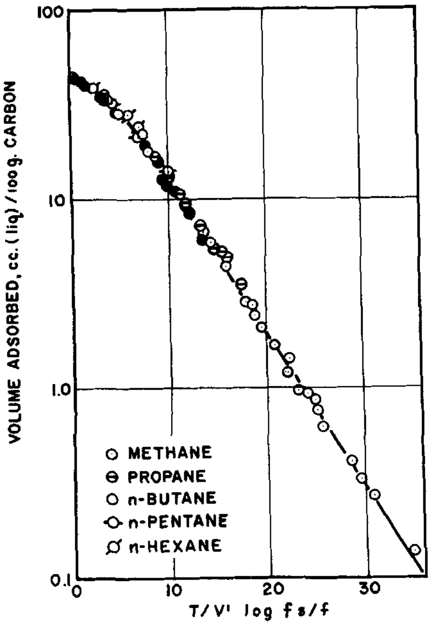

Fig. 10. Generalized adsorption correlation of normal paraffin hydrocarbons on BPL sample stock No. 2, 4 × 10 mesh.

sample of Pittsburgh carbon which they used. The data for paraffins on activated carbon confirms the predictive value of the correlation.

The sulfur gas correlation is shown in Figure 11. The degree of correlation here is not quite as good as for the hydrocarbons. Moreover the points from the 32.8° and 100°C. hydrogen sulfide disulfide isotherms are not included, because the values are much too high, as can be seen from the isotherms in Figure 7. The upward deviation may be attributed to chemisorption with oxygen complexes not removed by degassing. The high temperature *n*-propyl mercaptan isotherm (Figure 6) is too low without apparent reason. The remaining data show an approximate standard deviation of ±15% of the true value.

Separate correlation curves were found for the paraffins and the sulfur gases. Since the sulfur gas and the paraffin series were carried out on different samples of carbon, it was necessary to demonstrate that the adsorbents were equivalent. This was done by determining propane isotherms on the carbon used in the sulfur gas series, which agreed closely with the propane isotherms in Figure 2. The difference in the correlation curves is therefore real.

DISCUSSION

The abscissa in the generalized correlation is approximately the derivative of the excess adsorption energy with respect to occupied pore volume. This derivative in turn depends on the polarizability of individual bonds, the concentration at which they are packed into the pore volume, and the proximity of the adsorbate to the carbon. The proximity factor is the same for all adsorbates on a given carbon, at equal volumes adsorbed; its dependence on adsorbate volume is determined by the pore size distribution. This dependence may be treated by assuming a distribution function, in accordance with Dubinin *(15)*. Alternatively the correlation curve of Lewis et al. *(1)* determines in effect the volume dependence of the proximity factor for the carbon. In the hydrocarbon series the concentration of C—H bonds, and therefore the excess energy per unit volume, is largely independent of the size of the molecule. With other classes of compounds, such as the sulfur gases, one may expect a different correlation curve because of the different polarizability and density and therefore the different excess energy per unit volume. However, since the proximity factor remains the same on a given carbon, one should expect the excess adsorption energy for all adsorbates at equal volumes adsorbed to be equal except for a factor that is characteristic for each adsorbate and constant over a range of temperatures and pressures. Thus the hydrocarbon and the sulfur gas correlations can be made to coincide by a change in the abscissa scale. This suggests that having calibrated a carbon with one adsorbate (that does not exhibit hysteresis or chemisorption) one should be able to determine the adsorption isotherms of another adsorbate over a wide range of temperatures and pressures from a single experimental point which determines the appropriate scale for the abscissa.

Maslan et al. *(16)* have questioned the existence of an adsorbed liquid above its critical temperature and have correlated adsorption data on oxygen and nitrogen by assuming the adsorbates to be compressed gases. However propane adsorption did not correlate well by their method. The correlation of Lewis et al. *(1)*, on the other hand, appears to apply as well to methane (above critical temperature) as to the higher hydrocarbons (below critical temperature). In calculating the saturation fugacity of methane above its critical temperature the extrapolated values given by Maxwell *(5)* were used. The usual justification for the extrapolation above critical temperature is that the extrapolated data give valid results when used in liquid-vapor equilibrium calculations. The extrapolation appears to be useful in the present correlation as well. The difficulty of assigning a liquid density to an adsorbate above its critical temperature is neatly circumvented by the Lewis et al. *(1)* approximation provided only that the adsorption pressure is considerably less than the critical pressure. This embraces the region of practical interest.

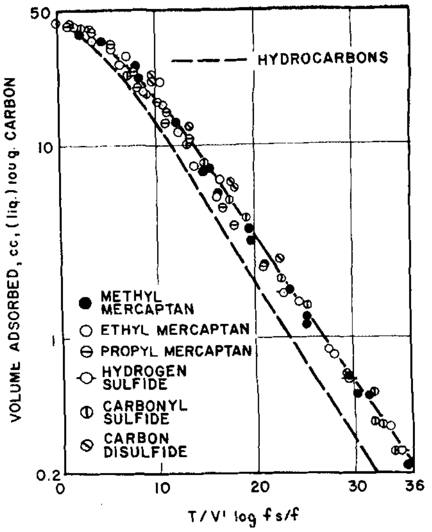

Fig. 11. Generalized adsorption correlation for sulfur gases on BPL 2026-54 (4 × 10) activated carbon.

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